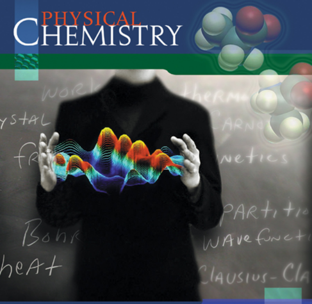
PHYSICAL CHEMISTRY



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Physical Chemistry

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Printed in the United States of America
1 2 3 4 5 6 7 06 05 04 03 02

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Library of Congress Control Number: 2002105398

ISBN 0-534-26658-4

THIS BOOK PRINTED ON ACID-FREE RECYCLED PAPER

Text Designer: Susan Schmidler
Photo Researcher: Linda L Rill
Copy Editor: Anita Wagner
Illustrator: Lotus Art
Cover Designer: Larry Didona
Cover Images: Teacher and blackboard: CORBIS; STM image of DNA: Lawrence Berkeley Lab/Photo Researchers; Molecular model: Kenneth Eward/BioGrafx/Photo Researchers
Compositor: ATLIS Graphics and Design
Text and Cover Printer: Quebecor World/Taunton

Brooks/Cole—Thomson Learning
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For my father

Contents

Preface

Subject: physical chemistry
"Is this subject hard?"
—*The entire text of a Usenet posting to* sci.chem, *September 1, 1994*

WHAT THIS PERSON'S QUESTION LACKED IN LENGTH, it made up for in angst. I spent almost an hour composing a response, which I posted. My response generated about half a dozen direct responses, all supporting my statements. Curiously, only half of the responses were from students; the other half were from professors.

Generally, I said that physical chemistry isn't inherently harder than any other technical subject. It *is* very mathematical, and students who may have formally satisfied the math requirements (typically calculus) may still find physical chemistry a challenge because it requires them to *apply* the calculus. Many instructors and textbooks can be overly presumptuous about the math abilities of the students, and consequently many students falter—not because they can't do the chemistry, but because they can't follow the math.

Also, in some cases the textbooks themselves are inappropriate for the level of a junior-year course (in my opinion). Many textbooks contain so much information that they blow the students away. Many of them are great books—for reference, on a professor's bookshelf, or for a graduate student studying for cumulative exams. But for undergraduate chemistry and chemical engineering majors taking physical chemistry for the first time? Too much! It's like using the *Oxford English Dictionary* as a text for English 101. Sure, the OED has all the vocabulary you would ever need, but it's overkill. Many physical chemistry texts are great for those who already know physical chemistry, but not for those who are trying to *learn* physical chemistry. What is needed is a book that works as a textbook, not as an encyclopedia, of physical chemistry.

This project is my attempt to address these ideas. *Physical Chemistry* is meant to be a *textbook* for the year-long, calculus-based physical chemistry course for science and engineering majors. It is meant to be used in its entirety, and it does not contain a lot of information (found in many other physical chemistry books) that undergraduate courses do not cover. There is some focus on mathematical manipulations because many students have forgotten how to apply calculus or could use the review. However, I have tried to keep in mind that this should be a physical chemistry text, not a math text.

Most physical chemistry texts follow a formula for covering the major topics: 1/3 thermodynamics, 1/3 quantum mechanics, and 1/3 statistical thermodynamics, kinetics, and various other topics. This text follows that general formula. The section on thermodynamics starts with gases and ends in electrochemistry, which is a fairly standard range of topics. The eight-chapter section on quantum mechanics and its applications to atoms and molecules starts on a more historical note. In my experience, students have little or no idea of why quantum mechanics was developed, and consequently they never recognize its importance, conclusions, or even its necessity. Therefore, Chapter 9 focuses on pre-quantum mechanics so students can develop an understanding of the state of classical science and how it could not explain the universe. This leads into an introduction to quantum mechanics and how it provides a useful model. Several chapters of symmetry and spectroscopy follow. In the last six chapters, this text covers statistical thermodynamics (intentionally not integrated with phenomenological thermodynamics), kinetic theory, kinetics, crystals, and surfaces. The text does not have separate chapters on photochemistry, liquids, molecular beams, thermal physics, polymers, and so on (although these topics may be mentioned throughout the text). This is not because I find these topics unimportant; I simply do not think that they must be included in an undergraduate physical chemistry textbook.

Each chapter opens with a synopsis of what the chapter will cover. In other texts, the student reads along blindly, not knowing where all the derivations and equations are leading. Indeed, other texts have a summary at the end of the chapters. In this text, a summary is given at the beginning of the chapter so the students can see where they are going and why. Numerous examples are sprinkled throughout all of the chapters, and there is an emphasis on the *units* in a problem, which are just as important as the numbers.

Exercises at the end of each chapter are separated by section so the student can better coordinate the chapter material with the problem. There are over 1000 end-of-chapter exercises to give students an opportunity to practice the concepts from the text. Although some mathematical derivations are included in the exercises, the emphasis is on exercises that make the students *use* the concepts, rather than just derive them. This, too, has been intentional on my part. Many answers to the exercises are included in an answer section at the back of the book. There are also end-of-chapter exercises that require symbolic mathematics software like MathCad or Maple (or even a high-level calculator), to practice some manipulations of the concepts. Only a few per chapter, they require more advanced skills and can be used as group assignments.

For a school on the quarter system, the material in physical chemistry almost naturally separates itself into three sections: thermodynamics (Chapters 1–8), quantum mechanics (Chapters 9–16), and other topics (Chapters 17–22). For a school on the semester system, instructors might want to consider pairing the thermodynamics chapters with the later chapters on kinetic theory (Chapter 19) and kinetics (Chapter 20) in the first term, and including Chapters 17 and 18 (statistical thermodynamics) and Chapters 21 and 22 (crystalline solids and surfaces) with the quantum mechanics chapters in the second term.

Professors: For a year-long sequence, you should be able to cover the *entire* book (and feel free to supplement with special topics as you see fit).

Students: For a year-long sequence, you should be able to read the *entire* book. You, too, can do it.

If you want an encyclopedia of physical chemistry, this is not the book for you. Other well-known books will serve that need. My hope is that students and teachers alike will appreciate this as a *textbook* of physical chemistry.

Acknowledgments

No project of this magnitude is the effort of one person. Chris Conti, a former editor for West Publishing, was enthusiastic about my ideas for this project long before anything was written down. His expressions of enthusiasm and moral support carried me through long periods of indecision. Lisa Moller and Harvey Pantzis, with the help of Beth Wilbur, got this project rolling at Brooks/Cole. They moved on to other things soon after I started, but I was fortunate to get Keith Dodson to serve as developmental editor. His input, guidance, and suggestions were appreciated. Nancy Conti helped with all the paper-shuffling and reviewing, and Marcus Boggs and Emily Levitan were there to see this project to its final production. I am in awe of the talents of Robin Lockwood (production editor), Anita Wagner (copy editor), and Linda Rill (photo editor). They made me feel as if I were the weakest link on the team (perhaps as it should be). There are undoubtedly many others at Brooks/Cole who are leaving their indelible mark on this text. Thanks to everyone for their assistance.

At various stages in its preparation, the entire manuscript was class-tested by students in several physical chemistry offerings at my university. Their feedback was crucial to this project, since you don't know how good a book is until you actually use it. Use of the manuscript wasn't entirely voluntary on their part (although they could have taken the course from some other instructor), but most of the students took on the task in good spirits and provided some valuable comments. They have my thanks: David Anthony, Larry Brown, Robert Coffman, Samer Dashi, Ruot Duany, Jim Eaton, Gianina Garcia, Carolyn Hess, Gretchen Hung, Ed Juristy, Teresa Klun, Dawn Noss, Cengiz Ozkose, Andrea Paulson, Aniko Prisko, Anjeannet Quint, Doug Ratka, Mark Rowitz, Yolanda Sabur, Prabhjot Sahota, Brian Schindly, Lynne Shiban, Tony Sinito, Yelena Vayner, Scott Wisniewski, Noelle Wojciechowicz, Zhiping Wu, and Steve Zamborsky. I would like to single out the efforts of Linnea Baudhuin, a student who performed one of the more comprehensive evaluations of the entire manuscript.

I would like to thank my faculty colleagues Tom Flechtner, Earl Mortensen, Bob Towns, and Yan Xu for their support. One regret is that my late colleague John Luoma, who read several parts of the manuscript and made some very helpful suggestions, did not see this project to its end. My appreciation also goes to the College of Arts and Science, Cleveland State University, for support of a two-quarter sabbatical during which I was able to make substantial progress on this project.

External reviewers gave feedback at several stages. I might not have always followed their suggestions, but their constructive criticism was appreciated. Thanks to:

Samuel A. Abrash, University of Richmond
Steven A. Adelman, Purdue University
Shawn B. Allin, Lamar University
Stephan B. H. Bach, University of Texas at San Antonio
James Baird, University of Alabama in Huntsville
Robert K. Bohn, University of Connecticut
Kevin J. Boyd, University of New Orleans
Linda C. Brazdil, Illinois Mathematics and Science Academy
Thomas R. Burkholder, Central Connecticut State University
Paul Davidovits, Boston College
Thomas C. DeVore, James Madison University
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Donald H. Secrest, University of Illinois at Urbana at Champaign
Michael P. Setter, Ball State University
Russell Tice, California Polytechnic State University
Edward A. Walters, University of New Mexico
Scott Whittenburg, University of New Orleans
Robert D. Williams, Lincoln University

I am indebted to Tom Burkholder of Central Connecticut State University and Mark Waner of John Carroll University for their assistance in performing accuracy reviews.

In a project such as this, it is extremely unlikely that perfection has been attained, so I would be grateful to anyone who points out any typo or misprint.

Finally, thanks to my wife Gail, who endured many an evening with me pounding away at the word processor instead of our sharing a few relaxing hours together. I hope you think it was worth it, after all.

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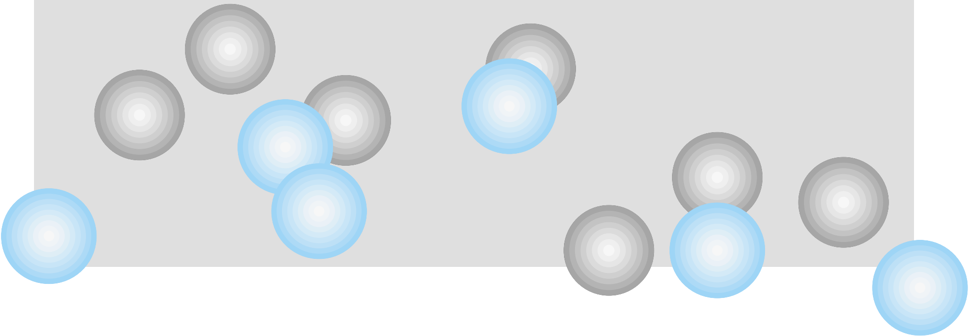
Physical Chemistry

1

Gases and the Zeroth Law of Thermodynamics



MUCH OF PHYSICAL CHEMISTRY CAN BE PRESENTED IN A DEVELOPMENTAL MANNER: one can grasp the easy ideas first and then progress to the more challenging ideas, which is similar to how these ideas were developed in the first place. Two of the major topics of physical chemistry—thermodynamics and quantum mechanics—lend themselves naturally to this approach.

In this first chapter on physical chemistry, we revisit a simple idea from general chemistry: gas laws. Gas laws—straightforward mathematical expressions that relate the observable properties of gases—were among the first quantifications of chemistry, dating from the 1600s, a time when the ideas of alchemy ruled. Gas laws provided the first clue that quantity, *how much,* is important in understanding nature. Some gas laws like Boyle's, Charles's, Amontons's, and Avogadro's laws are simple mathematically. Others can be very complex.

In chemistry, the study of large, or macroscopic, systems involves thermodynamics; in small, or microscopic, systems, it can involve quantum mechanics. In systems that change their structures over time, the topic is kinetics. But they all have basic connections with thermodynamics. We will begin the study of physical chemistry with thermodynamics.

1.1 Synopsis

This chapter starts with some definitions, an important one being the thermodynamic *system,* and the macroscopic variables that characterize it. If we are considering a gas in our system, we will find that various mathematical relationships are used to relate the physical variables that characterize this gas. Some of these relationships—"gas laws"—are simple but inaccurate. Other gas laws are more complicated but more accurate. Some of these more complicated gas laws have experimentally determined parameters that are tabulated to be looked up later, and they may or may not have physical justification. Finally, we develop some relationships (mathematical ones) using some simple calculus. These mathematical manipulations will be useful in later chapters as we get deeper into thermodynamics.

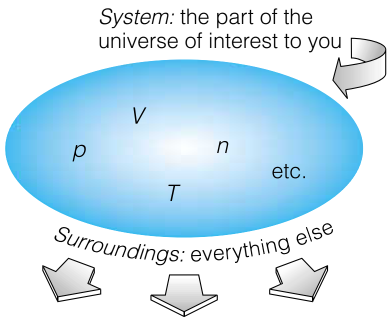


Figure 1.1 The system is the part of the universe of interest, and its state is described using macroscopic variables like pressure, volume, temperature, and moles. The surroundings are everything else. As an example, a system could be a refrigerator and the surroundings could be the rest of the house (and the surrounding space).

1.2 System, Surroundings, and State

Imagine you have a container holding some material of interest to you, as in Figure 1.1. The container does a good job of separating the material from everything else. Imagine, too, that you want to make measurements of the properties of that material, independent from the measurements of everything else around it. The material of interest is defined as the *system*. The "everything else" is defined as the *surroundings*. These definitions have an important function because they specify what part of the universe we are interested in: the system. Furthermore, using these definitions, we can immediately ask other questions: What interactions are there between the system and the surroundings? What is exchanged between the system and the surroundings?

For now, we consider the system itself. How do we describe it? That depends on the system. For example, a glass of milk is described differently from the interior of a star. But for now, let us pick a simple system, chemically speaking.

Consider a system that consists of a pure gas. How can we describe this system? Well, the gas has a certain volume, a certain pressure, a certain temperature, a certain chemical composition, a certain number of atoms or molecules, a certain chemical reactivity, and so on. If we can measure, or even dictate, the values of those descriptors, then we know everything we need to know about the properties of our system. We say that we know the *state* of our system.

If the state of the system shows no tendency to change, we say that the system is *at equilibrium* with the surroundings.* The equilibrium condition is a fundamental consideration of thermodynamics. Although not all systems are at equilibrium, we almost always use equilibrium as a reference point for understanding the thermodynamics of a system.

There is one other characteristic of our system that we ought to know: its energy. The energy is related to all of the other measurables of our system (as the measurables are related to each other, as we will see shortly). The understanding of how the energy of a system relates to its other measurables is called *thermodynamics* (literally, "heat movement"). Although thermodynamics ("thermo") ultimately deals with energy, it deals with other measurables too, and so the understanding of how those measurables relate to each other is an aspect of thermodynamics.

How do we define the state of our system? To begin, we focus on its physical description, as opposed to the chemical description. We find that we are able to describe the macroscopic properties of our gaseous system using only a few observables: they are the system's pressure, temperature, volume, and amount of matter (see Table 1.1). These measurements are easily identifiable and have well-defined units. Volume has common units of liter, milliliter, or cubic centimeter. [The cubic meter is the *Système International* (SI) unit of volume but these other units are commonly used as a matter of convenience.] Pressure has common units of atmosphere, torr, pascal (1 pascal = 1 N/m^2 and is the SI unit for pressure), or bar. Volume and pressure also have obvious minimum values against which a scale can be based. Zero volume and zero pressure are both easily definable. Amount of material is similar. It is easy to specify an amount in a system, and having nothing in the system corresponds to an amount of zero.

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*Equilibrium can be a difficult condition to define for a system. For example, a mixture of H_2 and O_2 gases may show no noticeable tendency to change, but it is not at equilibrium. It's just that the reaction between these two gases is so slow at normal temperatures and in the absence of a catalyst that there is no perceptible change.

Table 1.1 Common state variables and their units

Variable	Symbol	Common units
Pressure	p	Atmosphere, atm (= 1.01325 bar)
		Torricelli, torr (= $\frac{1}{760}$ atm)
		Pascal (SI unit)
		Pascal, Pa (= $\frac{1}{100{,}000}$ bar)
		Millimeters of mercury, mmHg (= 1 torr)
Volume	V	Cubic meter, m^3 (SI unit)
		Liter, L (= $\frac{1}{1000}$ m^3)
		Milliliter, mL (= $\frac{1}{1000}$ L)
		Cubic centimeter, cm^3 (= 1 mL)
Temperature	T	Degrees Celsius, °C, or kelvins, K
		°C = K − 273.15
Amount	n	Moles (can be converted to grams using molecular weight)

The temperature of a system has not always been an obvious measurable of a system, and the concept of a "minimum temperature" is relatively recent. In 1603, Galileo was the first to try to quantify changes in temperature with a water thermometer. Gabriel Daniel Fahrenheit devised the first widely accepted numerical temperature scale after developing a successful mercury thermometer in 1714, with zero set at the lowest temperature he could generate in his lab. Anders Celsius developed a different scale in 1742 in which the zero point was set at the freezing point of water. These are *relative,* not *absolute,* temperatures. Warmer and colder objects have a temperature value in these relative scales that is decided with respect to these and other defined points in the scale. In both cases, temperatures lower than zero are possible and so the temperature of a system can sometimes be reported as a negative value. Volume, pressure, and amount cannot have a negative value, and later we define a temperature scale that cannot, either. Temperature is now considered a well-understood variable of a system.

1.3 The Zeroth Law of Thermodynamics

Thermodynamics is based on a few statements called *laws* that have broad application to physical and chemical systems. As simple as these laws are, it took many years of observation and experimentation before they were formulated and recognized as scientific laws. Three such statements that we will eventually discuss are the first, second, and third laws of thermodynamics.

However, there is an even more fundamental idea that is usually assumed but rarely stated because it is so obvious. Occasionally this idea is referred to as the zeroth law of thermodynamics, since even the first law depends on it. It has to do with one of the variables that was introduced in the previous section, temperature.

What is temperature? *Temperature is a measure of how much kinetic energy the particles of a system have.* The higher the temperature, the more energy a system has, all other variables defining the state of the system (volume, pressure, and so on) being the same. Since thermodynamics is in part the study of energy, temperature is a particularly important variable of a system.

We must be careful when interpreting temperature, however. Temperature is *not* a form of energy. Instead, it is a parameter used to compare amounts of energy of different systems.

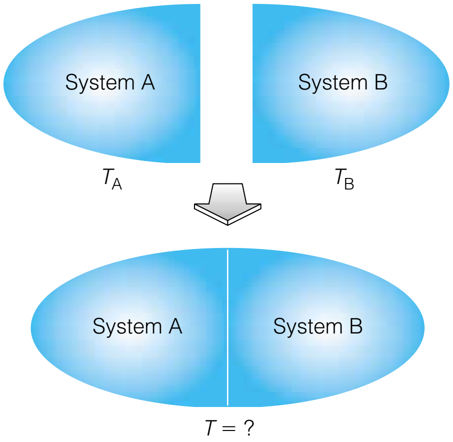

Figure 1.2 What happens to the temperature when two individual systems are brought together?

Consider two systems, A and B, in which the temperature of A is greater than the temperature of B (Figure 1.2). Each is a *closed system*, which means that matter cannot move in or out of each system but energy can. The state of each system is defined by quantities like pressure, volume, and temperature. The two systems are brought together and physically joined but kept separate from each other, as shown. For example, two pieces of metal can be brought into contact with each other, or two containers of gas can be connected by a closed stopcock. Despite the connection, matter will not be exchanged between the two systems or with the surroundings.

What about their temperatures, T_A and T_B? What is always observed is that energy transfers from one system to another. As energy transfers between the two systems, the two temperatures change until the point where $T_A = T_B$. At that point, the two systems are said to be at *thermal equilibrium*. Energy may still transfer between the systems, but the *net* change in energy will be zero and the temperature will not change further. The establishment of thermal equilibrium is independent of the system size. It applies to large systems, small systems, and any combination of large and small systems.

The transfer of energy from one system to another due to temperature differences is called *heat*. We say that heat has flowed from system A to system B. Further, if a third system C is in thermal equilibrium with system A, then $T_C = T_A$ and system C must be in thermal equilibrium with system B also. This idea can be expanded to include any number of systems, but the basic idea illustrated by three systems is summed up by a statement called the zeroth law of thermodynamics:

> The zeroth law of thermodynamics: If two systems (of any size) are in thermal equilibrium with each other and a third system is in thermal equilibrium with one of them, then it is in thermal equilibrium with the other also.

This is obvious from personal experience, and fundamental to thermodynamics.

Example 1.1

Consider three systems at 37.0°C: a 1.0-L sample of H_2O, 100 L of neon gas at 1.00 bar pressure, and a small crystal of sodium chloride, NaCl. Comment on their thermal equilibrium status in terms of the varying sizes of the systems. Will there be any net transfer of energy if they are brought into contact?

Solution

Thermal equilibrium is dictated by the temperature of the systems involved, not the sizes. Since all systems are at the same temperature [that is, $T(H_2O) = T(Ne) = T(NaCl)$], they are all in thermal equilibrium with each other. To invoke the zeroth law, if the water is in thermal equilibrium with the neon and the neon is in thermal equilibrium with the sodium chloride, then the water is in thermal equilibrium with the sodium chloride. No matter what the relative sizes of the systems are, there should be no net transfer of energy between any of the three systems.

The zeroth law introduces a new idea. One of the variables that defines the state of our system (the *state variables*) changes its value. In this case, the temperature has changed. We are ultimately interested in how the state variables change and how these changes relate to the energy of our system.

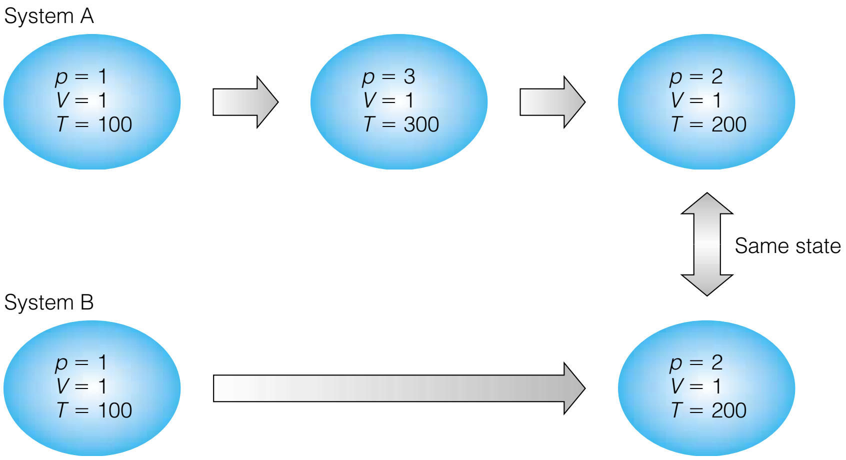

Figure 1.3 The state of a system is determined by what the state variables *are,* not how the system got there. In this example, the initial and final states of the two Systems (A) and (B) are the same, regardless of the fact that System (A) was higher in temperature and pressure in the interim.

The final point with respect to the system and its variables is the fact that the system does not remember its previous state. The state of the system is dictated by the values of the state variables, not their previous values or how they changed. Consider the two systems in Figure 1.3. System A goes to a higher temperature before settling on $T = 200$ temperature units. System B goes directly from the initial conditions to the final conditions. Therefore, the two states are the same. It does not matter that the first system was at a higher temperature; the state of the system is dictated by what the state variables are, not what they were, or how they got there.

1.4 Equations of State

Phenomenological thermodynamics is based on *experiment,* on measurements that you might make in a lab, garage, or kitchen. For example, for any fixed amount of a pure gas, two state variables are pressure, p, and volume, V. Each can be controlled independently of each other. The pressure can be varied while the volume is kept constant, or vice versa. Temperature, T, is another state variable that can be changed independently from p and V. However, experience has shown that if a certain pressure, volume, and temperature were specified for a particular sample of gas at equilibrium, then all measurable, macroscopic properties of that sample have certain specific values. That is, these three state variables determine the complete state of our gas sample. Notice that we are implying the existence of one other state variable: amount. The amount of material in the system, designated by n, is usually given in units of moles.

Further, arbitrary values for all four variables p, V, n, and T are not possible simultaneously. Again, experience (that is, experiment) shows this. It turns out that only two of the three state variables p, V, and T are truly independent for any given amount of a gas. Once two values are specified, then the third one must have a certain value. This means that there is a mathematical equation into which we can substitute for two of the variables and calculate what the remaining variable must be. Say such an equation requires that we know p and V and lets us calculate T. Mathematically, there exists some function F such that

$$F(p, V) = T \quad \text{at fixed } n \tag{1.1}$$

where the function is written as $F(p, V)$ to emphasize that the variables are pressure and volume, and that the outcome yields the value of the temperature T. Equations like equation 1.1 are called *equations of state*. One can also define equations of state that yield p or V instead of T. In fact, many equations of state can be algebraically rearranged to yield one of several possible state variables.

The earliest equations of state for gases were determined by Boyle, Charles, Amontons, Avogadro, Gay-Lussac, and others. We know these equations as the various *gas laws*. In the case of Boyle's gas law, the equation of state involves multiplying the pressure by the volume to get a number whose value depended on the temperature of the gas:

$$p \cdot V = F(T) \quad \text{at fixed } n \tag{1.2}$$

whereas Charles's gas law involves volume and temperature:

$$\frac{V}{T} = F(p) \quad \text{at fixed } n \tag{1.3}$$

Avogadro's law relates volume and amount, but at fixed temperature and pressure:

$$V = F(n) \quad \text{at fixed } T, p \tag{1.4}$$

In the above three equations, if the temperature, pressure, or amount were kept constant, then the respective functions $F(T)$, $F(p)$, and $F(n)$ would be constants. This means that if one of the state variables that can change does, the other must also change in order for the gas law to yield the same constant. This leads to the familiar predictive ability of the above gas laws using the forms

$$p_1V_1 = F(T) = p_2V_2 \quad \text{or} \quad p_1V_1 = p_2V_2 \tag{1.5}$$

Similarly, using equations 1.3 and 1.4, we can get

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \tag{1.6}$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \tag{1.7}$$

All three gas laws involve volume, and they can be rewritten as

$$V \propto \frac{1}{p}$$

$$V \propto T$$

$$V \propto n$$

where the symbol ∝ means "is proportional to." We can combine the three proportionalities above into one:

$$V \propto \frac{nT}{p} \tag{1.8}$$

Since p, V, T, and n are the only four independent state variables for a gas, the proportionality form of equation 1.8 can be turned into an equality by using a proportionality constant:

$$V = R \cdot \frac{nT}{p} \tag{1.9}$$

where we use R to represent the proportionality constant. This equation of state relates the static (unchanging) values of p, V, T, and n, not changes in these values. It is usually rewritten as

$$pV = nRT \tag{1.10}$$

which is the familiar *ideal gas law,* with R being the *ideal gas law constant.*

At this point, we must return to a discussion of temperature units and introduce the proper thermodynamic temperature scale. It has already been mentioned that the Fahrenheit and Celsius temperature scales have arbitrary zero points. What is needed is a temperature scale that has an absolute zero point that is physically relevant. Values for temperature can then be scaled from that point. In 1848, the British scientist William Thomson (Figure 1.4), later made a baron and taking the title Lord Kelvin, considered the temperature-volume relationship of gases and other concerns (some of which we will address in future chapters) and proposed an absolute temperature scale where the minimum possible temperature is about −273°C, or 273 Celsius-sized degrees below the freezing point of water. [A modern value is −273.15°C, and is based on the triple point (discussed in Chapter 6) of H_2O, not the freezing point.] A scale was established by making the degree size for this absolute scale the same as the Celsius scale. In thermodynamics, gas temperatures are almost always expressed in this new scale, called the *absolute scale* or the *Kelvin scale,* and the letter K is used (without a degree sign) to indicate a temperature in kelvins. Because the degree sizes are the same, there is a simple conversion between a temperature in degrees Celsius and the same temperature in kelvins:

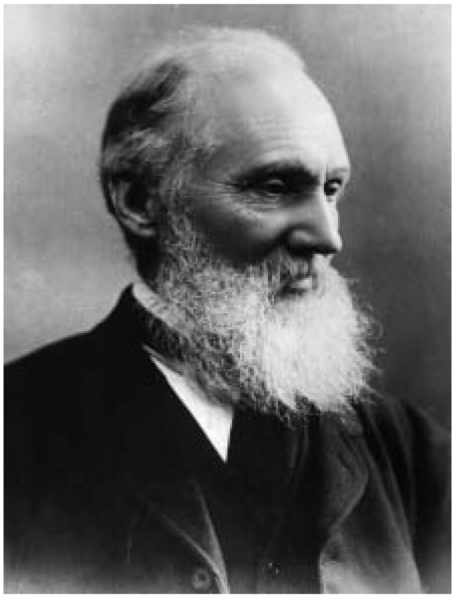

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Figure 1.4 William Thomson, later Baron Kelvin (1824–1907), a Scottish physicist. Thomson established the necessity of a minimum absolute temperature, and proposed a temperature scale based on that absolute zero. He also performed valuable work on the first transatlantic cable. Thomson was made a baron in 1892 and borrowed the name of the Kelvin River. Because he left no heirs, there is no current Baron Kelvin.

$$\mathrm{K} = {}^{\circ}\mathrm{C} + 273.15 \tag{1.11}$$

Occasionally, the conversion is truncated to three significant figures and becomes simply K = °C + 273.

In all of the gas laws given above, *the temperature must be expressed in kelvins!* The absolute temperature scale is the only appropriate scale for thermodynamic temperatures. (For *changes* in temperature, the units can be kelvins or degrees Celsius, since the change in temperature will be the same. However, the absolute value of the temperature will be different.)

Having established the proper temperature scale for thermodynamics, we can return to the constant R. This value, the ideal gas law constant, is probably the most important physical constant for macroscopic systems. Its specific numerical value depends on the units used to express the pressure and volume, since the units in an equation must also satisfy certain algebraic necessities. Table 1.2 lists various values of R. The ideal gas law is the best-known equation of state for a gaseous system. Gas systems whose state variables p, V, n, and T vary according to the ideal gas law satisfy one criterion of an *ideal gas* (the other criterion is presented in Chapter 2). *Real gases,* which do not follow the ideal gas law exactly, can approximate ideal gases if they are kept at high temperature and low pressure.

Table 1.2 Values for R, the ideal gas law constant

R = 0.08205 L·atm/mol·K
0.08314 L·bar/mol·K
1.987 cal/mol·K
8.314 J/mol·K
62.36 L·torr/mol·K

It is useful to define a set of reference state variables for gases, since they can have a wide range of values that can in turn affect other state variables. The most common set of reference state variables for pressure and temperature is p = 1.0 atm and T = 273.15 K = 0.0°C. These conditions are called *standard temperature and pressure,* abbreviated STP. Much of the thermodynamic data reported for gases are given for conditions of STP. SI also defines *standard ambient temperature and pressure,* SATP, as 273.15 K for temperature and 1 bar for pressure (1 bar = 0.987 atm).

Example 1.2

Calculate the volume of 1 mole of an ideal gas at SATP.

Solution

Using the ideal gas law and the appropriate value for R:

$$V = \frac{nRT}{P} = \frac{(1\ \text{mol})(0.08314\ \frac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}})(273.15\ \text{K})}{1\ \text{bar}}$$

$$V = 22.71\ \text{L}$$

This is slightly larger than the commonly used molar volume of a gas at STP (about 22.4 L), since the pressure is slightly lower.

1.5 Partial Derivatives and Gas Laws

A major use of equations of state in thermodynamics is to determine how one state variable is affected when another state variable changes. In order to do this, we need the tools of calculus. For example, a straight line, as in Figure 1.5a, has a slope given by $\Delta y/\Delta x$, which in words is simply "the change in y as x changes." For a straight line, the slope is the same everywhere on the line. For curved lines, as shown in Figure 1.5b, the slope is constantly changing. Instead of writing the slope of the curved line as $\Delta y/\Delta x$, we use the symbolism of calculus and write it as dy/dx, and we call this "the derivative of y with respect to x."

Equations of state deal with many variables. The *total derivative* of a function of multiple variables, $F(x, y, z, \ldots)$, is defined as

$$dF = \left(\frac{\partial F}{\partial x}\right)_{y,z,\ldots} dx + \left(\frac{\partial F}{\partial y}\right)_{x,z,\ldots} dy + \left(\frac{\partial F}{\partial z}\right)_{x,y,\ldots} dz + \cdots \quad \textbf{(1.12)}$$

In equation 1.12, we are taking the derivative of the function F with respect to one variable at a time. In each case, the other variables are held constant. Thus, in the first term, the derivative

$$\left(\frac{\partial F}{\partial x}\right)_{y,z,\ldots} \quad \textbf{(1.13)}$$

is the derivative of the function F with respect to x only, and the variables y, z, and so on are treated as constants. Such a derivative is a *partial derivative*. The total derivative of a multivariable function is the sum of all of its partial

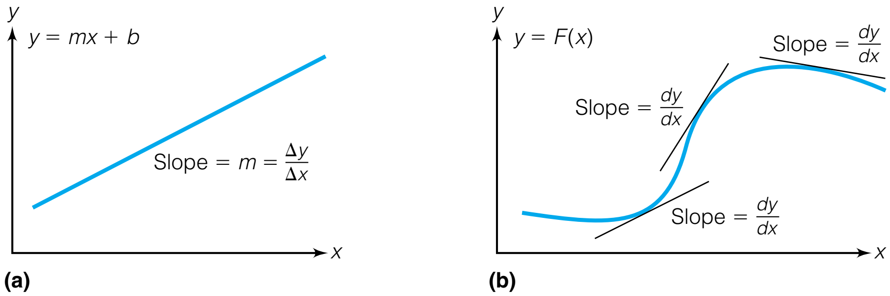


Figure 1.5 (a) Definition of slope for a straight line. The slope is the same at every point on the line. (b) A curved line also has a slope, but it changes from point to point. The slope of the line at any particular point is determined by the derivative of the equation for the line.

derivatives, each multiplied by the infinitesimal change in the appropriate variable (given as dx, dy, dz, and so on in equation 1.12).

Using equations of state, we can take derivatives and determine expressions for how one state variable changes with respect to another. Sometimes these derivatives lead to important conclusions about the relationships between the state variables, and this can be a powerful technique in working with thermodynamics.

For example, consider our ideal gas equation of state. Suppose we need to know how the pressure varies with respect to temperature, assuming the volume and number of moles in our gaseous system remain constant. The partial derivative of interest can be written as

$$\left(\frac{\partial p}{\partial T}\right)_{V,n}$$

Several partial derivatives relating the different state variables of an ideal gas can be constructed, some of which are more useful or understandable than others. However, any derivative of R is zero, because R is a constant.

Because we have an equation that relates p and T—the ideal gas law—we can evaluate this partial derivative analytically. The first step is to rewrite the ideal gas law so that pressure is all by itself on one side of the equation. The ideal gas law becomes

$$p = \frac{nRT}{V}$$

The next step is to take the derivative of both sides with respect to T, while treating everything else as a constant. The left side becomes

$$\left(\frac{\partial p}{\partial T}\right)_{V,n}$$

which is the partial derivative of interest. Taking the derivative of the right side:

$$\frac{\partial}{\partial T}\left(\frac{nRT}{V}\right) = \frac{nR}{V}\frac{\partial}{\partial T}T = \frac{nR}{V}\cdot 1 = \frac{nR}{V}$$

Combining the two sides:

$$\left(\frac{\partial p}{\partial T}\right)_{V,n} = \frac{nR}{V} \tag{1.14}$$

That is, from the ideal gas law, we are able to determine how one state variable varies with respect to another in an analytic fashion (that is, with a specific mathematical expression). A plot of pressure versus temperature is shown in Figure 1.6. Consider what equation 1.14 is telling you. A derivative is a *slope*. Equation 1.14 gives you the plot of pressure (y-axis) versus temperature (x-axis). If you took a sample of an ideal gas, measured its pressure at different temperatures but at constant volume, and plotted the data, you would get a straight line. The slope of that straight line should be equal to nR/V. The numerical value of this slope would depend on the volume and number of moles of the ideal gas.

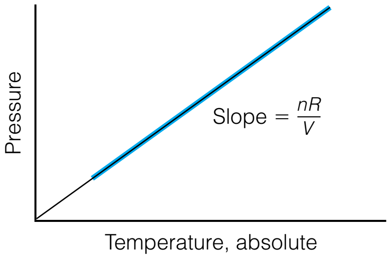


Figure 1.6 Plotting the pressure of a gas versus its absolute temperature, one gets a straight line whose slope equals nR/V. Algebraically, this is a plot of the equation $p = (nR/V) \cdot T$. In calculus terms, the slope of this line is $(\partial p/\partial T)_{V,n}$ and is constant.

Example 1.3

Determine the change of pressure with respect to volume, all else remaining constant, for an ideal gas.

Solution

The partial derivative of interest is

$$\left(\frac{\partial p}{\partial V}\right)_{T,n}$$

which we can evaluate in a fashion similar to the example above, using

$$p = \frac{nRT}{V}$$

only this time taking the derivative with respect to V instead of T. Following the rules of taking derivatives, and treating n, R, and T as constants, we get

$$\left(\frac{\partial p}{\partial V}\right)_{T,n} = -\frac{nRT}{V^2}$$

for this change. Notice that although in our earlier example the change did not depend on T, here the change in p with respect to V depends on the instantaneous value of V. A plot of pressure versus volume will *not* be a straight line. (Determine the numerical value of this slope for 1 mole of gas having a volume of 22.4 L at a temperature of 273 K. Are the units correct?)

Substituting values into these expressions for the slope must give units that are appropriate for the partial derivative. For example, the actual numerical value of $(\partial p/\partial T)_{V,n}$, for $V = 22.4$ L and 1 mole of gas, is 0.00366 atm/K. The units are consistent with the derivative being a change in pressure (units of atm) with respect to temperature (units of K). Measurements of gas pressure versus temperature at a known, constant volume can in fact provide an experimental determination of the ideal gas law constant R. This is one reason why partial derivatives of this type are useful. They can sometimes provide us with ways of measuring variables or constants that might be difficult to determine directly. We will see more examples of that in later chapters, all ultimately deriving from partial derivatives of just a few simple equations.

Finally, the derivative in Example 1.3 suggests that any true ideal gas goes to zero volume at 0 K. This ignores the fact that atoms and molecules themselves have volume. However, gases do not act very ideally at such low temperatures anyway.

1.6 Nonideal Gases

Under most conditions, the gases that we deal with in reality deviate from the ideal gas law. They are real gases, not ideal gases. Figure 1.7 shows the behavior of a real gas compared to an ideal gas. The behavior of real gases can also be described using equations of state, but as might be expected, they are more complicated.

Let us first consider 1 mole of gas. If it is an ideal gas, then we can rewrite the ideal gas law as

$$\frac{p\overline{V}}{RT} = 1 \tag{1.15}$$

where $\overline{V}$ is the *molar volume* of the gas. (Generally, any state variable that is written with a line over it is considered a molar quantity.) For a nonideal gas,

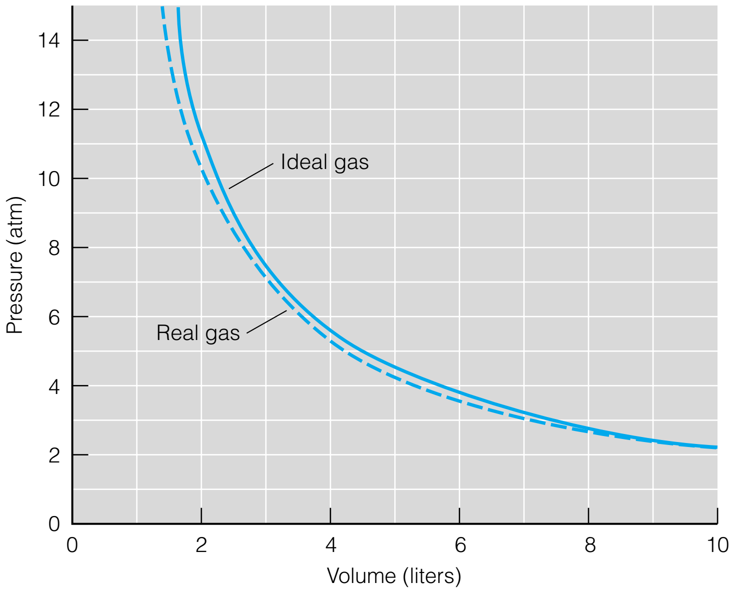


Figure 1.7 The $p - V$ behavior of an ideal gas compared to a real gas.

this quotient may not equal 1. It can also be less than or greater than 1. Therefore, the above quotient is defined as the *compressibility factor Z:*

$$Z \equiv \frac{p\overline{V}}{RT} \tag{1.16}$$

Specific values for compressibility depend on the pressure, volume, and temperature of the real gas, but generally, the farther Z is from 1, the less ideally the gas behaves. Figure 1.8 shows two plots of compressibility, one with respect to pressure and another with respect to temperature.

It would be extremely useful to have mathematical expressions that provide the compressibilities (and therefore an idea of the behavior of the gas toward changing state variables). These expressions are equations of state for the real gases. One common form for an equation of state is called a *virial equation. Virial* comes from the Latin word for "force" and implies that gases are nonideal because of the forces between the atoms or molecules. A virial equation is simply a power series in terms of one of the state variables, either p or $\overline{V}$. (Expressing a measurable, in this case the compressibility, in terms of a power series is a common tactic in science.) Virial equations are one way to fit the behavior of a real gas to a mathematical equation.

In terms of volume, the compressibility of real gases can be written as

$$Z = \frac{p\overline{V}}{RT} = 1 + \frac{B}{\overline{V}} + \frac{C}{\overline{V}^2} + \frac{D}{\overline{V}^3} + \cdots \tag{1.17}$$

where B, C, D, . . . are called the *virial coefficients* and are dependent on the nature of the gas and the temperature. The constant that would be labeled A is simply 1, so the virial coefficients "start" with B. B is called the *second* virial coefficient; C is the third virial coefficient, and so forth. Because the denominator, the power series in $\overline{V}$, gets larger and larger as the exponent increases, successive coefficients make a smaller and smaller contribution to the compressibility. The largest single correction is due to the B term, making it the

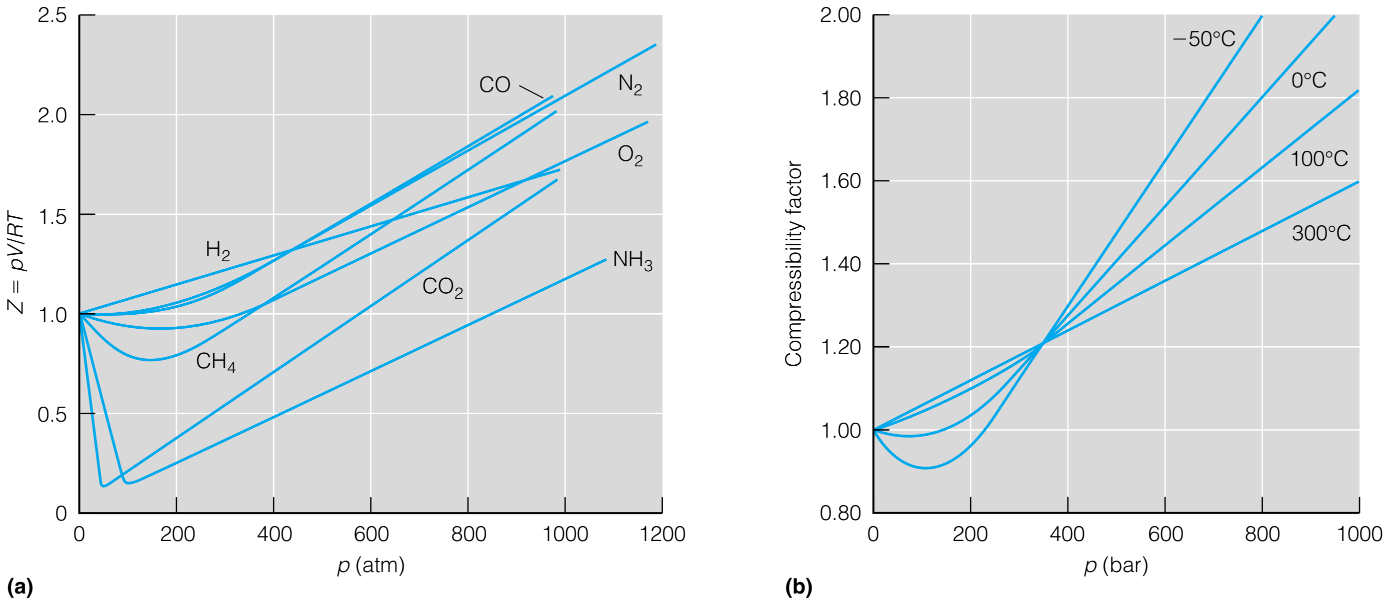


Figure 1.8 (a) Compressibilities of various gases at different pressures. (b) Compressibilities of nitrogen at different temperatures. Note that in both graphs, the compressibilities approach 1 at the limit of low pressure. (*Sources:* (a) J. P. Bromberg, *Physical Chemistry,* 2nd ed., Allyn & Bacon, Boston, 1980. Reprinted with permission of Pearson Education, Inc. Upper Saddle River, N.J. (b) R. A. Alberty, *Physical Chemistry,* 7th ed., Wiley, New York, 1987.)

Table 1.3 Second virial coefficients B for various gases (in cm^3/mol, at 300 K)

Gas	B
Ammonia, NH_3	−265
Argon, Ar	−16
Carbon dioxide, CO_2	−126
Chlorine, Cl_2	−299
Ethylene, C_2H_2	−139
Hydrogen, H_2	15
Methane, CH_4	−43
Nitrogen, N_2	−4
Oxygen, O_2	−16[a]
Sulfur hexafluoride, SF_6	−275
Water, H_2O	−1126

Source: D. R. Lide, ed., *CRC Handbook of Chemistry and Physics,* 82nd ed., CRC Press, Boca Raton, Fla., 2001.

[a] Extrapolated

most important measure of the nonideality of a real gas. Table 1.3 lists values of the second virial coefficient of several gases.

Virial equations of state in terms of pressure instead of volume are often written not in terms of compressibility, but in terms of the ideal gas law itself:

$$p\overline{V} = RT + B'p + C'p^2 + D'p^3 + \cdots \qquad \textbf{(1.18)}$$

where the primed virial coefficients *do not* have the same values as the virial coefficients in equation 1.17. However, if we rewrite equation 1.18 in terms of compressibility, we get

$$Z = \frac{p\overline{V}}{RT} = 1 + \frac{B'p}{RT} + \frac{C'p^2}{RT} + \frac{D'p^3}{RT} + \cdots \qquad \textbf{(1.19)}$$

At the limit of low pressures, it can be shown that $B = B'$. The second virial coefficient is typically the largest nonideal term in a virial equation, and many lists of virial coefficients give only B or B'.

Example 1.4

Using equations 1.17 and 1.19, show that B and B' have the same units.

Solution

Equation 1.17 implies that the compressibility is unitless, so the second virial coefficient must cancel out the unit in the denominator of the second term. Since volume is in the denominator, B must have units of volume. In equation 1.19, compressibility is again unitless, so the unit for B' must cancel out the collective units of p/RT. But p/RT has units of $(\text{volume})^{-1}$; that is, units of volume are in the denominator. Therefore, B' must provide units of volume in the numerator, so B' must also have units of volume.

Table 1.4 The second virial coefficient B (cm^3/mol) at various temperatures

Temperature (K)	He	Ne	Ar
20	−3.34	—	—
50	7.4	−35.4	—
100	11.7	−6.0	−183.5
150	12.2	3.2	−86.2
200	12.3	7.6	−47.4
300	12.0	11.3	−15.5
400	11.5	12.8	−1.0
600	10.7	13.8	12.0

Source: J. S. Winn, *Physical Chemistry,* HarperCollins, New York, 1994

Table 1.5 Boyle temperatures for various gases

Gas	T_B (K)
H_2	110
He	25
Ne	127
Ar	410
N_2	327
O_2	405
CO_2	713
CH_4	509

Source: J. S. Winn, *Physical Chemistry,* Harper Collins, New York, 1994

Because of the various algebraic relationships between the virial coefficients in equations 1.17 and 1.18, typically only one set of coefficients is tabulated and the other can be derived. Again, B (or B') is the most important virial coefficient, since its term makes the largest correction to the compressibility, Z.

Virial coefficients vary with temperature, as Table 1.4 illustrates. As such, there should be some temperature at which the virial coefficient B goes to zero. This is called the *Boyle temperature,* T_B, of the gas. At that temperature, the compressibility is

$$Z = \frac{p\overline{V}}{RT} + \frac{0}{\overline{V}} + \cdots$$

where the additional terms will be neglected. This means that

$$Z \approx \frac{p\overline{V}}{RT}$$

and the real gas is acting like an ideal gas. Table 1.5 lists Boyle temperatures of some real gases. The existence of Boyle temperature allows us to use real gases to study the properties of ideal gases—if the gas is at the right temperature, and successive terms in the virial equation are negligible.

One model of ideal gases is that (a) they are composed of particles so tiny compared to the volume of the gas that they can be considered zero-volume points in space, and (b) there are no interactions, attractive or repulsive, between the individual gas particles. However, real gases ultimately have behaviors due to the facts that (a) gas atoms and molecules *do* have a size, and (b) there is some interaction between the gas particles, which can range from minimal to very large. In considering the state variables of a gas, the volume of the gas particles should have an effect on the volume V of the gas. The interactions between gas particles would have an effect on the pressure p of the gas. Perhaps a better equation of state for a gas should take these effects into account.

Photo by Gen. Stab. Lit. Anst, courtesy AIP Emilio Segre Visual Archives, W. F. Meggers Gallery of Nobel Laureates and Weber Collection

Figure 1.9 Johannes van der Waals (1837–1923), Dutch physicist who proposed a new equation of state for gases. He won a 1910 Nobel Prize for his work.

In 1873, the Dutch physicist Johannes van der Waals (Figure 1.9) suggested a somewhat corrected version of the ideal gas law. It is one of the simpler equations of state for real gases, and is referred to as the *van der Waals equation:*

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT \tag{1.20}$$

where n is the number of moles of gas, and a and b are the *van der Waals constants* for a particular gas. The van der Waals constant a represents the pressure

Table 1.6 Van der Waals parameters for various gases

Gas	a (atm·L^2/mol^2)	b (L/mol)
Acetylene, C_2H_2	4.390	0.05136
Ammonia, NH_3	4.170	0.03707
Carbon dioxide, CO_2	3.592	0.04267
Ethane, C_2H_6	5.489	0.0638
Ethylene, C_2H_4	4.471	0.05714
Helium, He	0.03508	0.0237
Hydrogen, H_2	0.244	0.0266
Hydrogen chloride, HCl	3.667	0.04081
Krypton, Kr	2.318	0.03978
Mercury, Hg	8.093	0.01696
Methane, CH_4	2.253	0.0428
Neon, Ne	0.2107	0.01709
Nitric oxide, NO	1.340	0.02789
Nitrogen, N_2	1.390	0.03913
Nitrogen dioxide, NO_2	5.284	0.04424
Oxygen, O_2	1.360	0.03183
Propane, C_3H_8	8.664	0.08445
Sulfur dioxide, SO_2	6.714	0.05636
Xenon, Xe	4.194	0.05105
Water, H_2O	5.464	0.03049

Source: D. R. Lide, ed., *CRC Handbook of Chemistry and Physics,* 82nd ed., CRC Press, Boca Raton, Fla., 2001.

correction and is related to the magnitude of the interactions between gas particles. The van der Waals constant b is the volume correction and is related to the size of the gas particles. Table 1.6 lists van der Waals constants for various gases, which can be determined experimentally. Unlike a virial equation, which fits behavior of real gases to a mathematical equation, the van der Waals equation is a mathematical model that attempts to predict behavior of a gas in terms of real physical phenomena (that is, interaction between gas molecules and the physical sizes of atoms).

Example 1.5

Consider a 1.00-mole sample of sulfur dioxide, SO_2, that has a pressure of 5.00 atm and a volume of 10.0 L. Predict the temperature of this sample of gas using the ideal gas law and the van der Waals equation.

Solution

Using the ideal gas law, we can set up the following expression:

$$(5.00\text{ atm})(10.0\text{ L}) = (1.00\text{ mol})\left(0.08205\ \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(T)$$

and solve for T to get $T = 609$ K. Using the van der Waals equation, we first need the constants a and b. From Table 1.6, they are 6.714 atm·L^2/mol^2 and 0.05636 L/mol. Therefore, we set up

$$\left(5.00\text{ atm} + \frac{\left(6.714\ \frac{\text{atm}\cdot\text{L}^2}{\text{mol}^2}\right)(1\text{ mol})^2}{(10\text{ L})^2}\right)\left(10.0\text{ L} - 1.00\text{ mol}\left(0.05636\ \frac{\text{L}}{\text{mol}}\right)\right)$$

$$= (1.00\text{ mol})\left(0.08205\ \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(T)$$

Simplifying the left-hand side of the equation:

$$(5.00\text{ atm} + 0.06714\text{ atm})(10.0\text{ L} - 0.05636\text{ L}) = (1.00\text{ mol})\left(0.08205\ \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(T)$$

$$(5.067\text{ atm})(9.94\text{ L}) = (1.00\text{ mol})\left(0.08205\ \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(T)$$

Solving for T, one finds $T = 613$ K for the temperature of the gas, 4° higher than the ideal gas law.

The different equations of state are not always used independently of each other. We can derive some useful relationships by comparing the van der Waals equation with the virial equation. If we solve for p from the van der Waals equation and substitute it into the definition of compressibility, we get

$$Z = \frac{p\overline{V}}{RT} = \frac{\overline{V}}{\overline{V} - b} - \frac{a}{RT\overline{V}} \qquad \textbf{(1.21)}$$

which can be rewritten as

$$Z = \frac{1}{1 - b/\overline{V}} - \frac{a}{RT\overline{V}}$$

At very low pressures (which is one of the conditions under which real gases might behave somewhat like ideal gases), the volume of the gas system will be large (from Boyle's law). That means that the fraction $b/\overline{V}$ will be very small, and so using the Taylor-series approximation $1/(1 - x) = (1 - x)^{-1} \approx 1 + x + x^2 + \cdots$ for $x \ll$, we can substitute for $1/(1 - b/\overline{V})$ in the last expression to get

$$Z = 1 + \frac{b}{\overline{V}} + \left(\frac{b}{\overline{V}}\right)^2 - \frac{a}{RT\overline{V}} + \cdots$$

where successive terms are neglected. The two terms with $\overline{V}$ to the first power in their denominator can be combined to get

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\overline{V}} + \left(\frac{b}{\overline{V}}\right)^2 + \cdots$$

for the compressibility in terms of the van der Waals equation of state. Compare this to the virial equation of state in equation 1.17:

$$Z = \frac{p\overline{V}}{RT} = 1 + \frac{B}{\overline{V}} + \frac{C}{\overline{V}^2} + \cdots$$

By performing a power series term-by-term comparison, we can show a correspondence between the coefficients on the $1/\overline{V}$ term:

$$B = \left(b - \frac{a}{RT}\right) \tag{1.22}$$

We have therefore established a simple relationship between the van der Waals constants a and b and the second virial coefficient B. Further, since at the Boyle temperature T_B the second virial coefficient B is zero:

$$0 = b - \frac{a}{RT_B}$$

we can rearrange to find that

$$T_B = \frac{a}{bR} \tag{1.23}$$

This expression shows that all gases whose behavior can be described using the van der Waals equation of state (and most gases can, at least in certain regions of pressure and temperature) have a finite T_B and should behave like an ideal gas at that temperature, if higher virial equation terms are negligible.

Example 1.6

Estimate the Boyle temperature of the following. Use the values of a and b from Table 1.6.

a. He

b. Methane, CH_4

Solution

a. For He, $a = 0.03508$ atm·L^2/mol^2 and $b = 0.0237$ L/mol. The proper numerical value for R will be necessary to cancel out the right units; in this case, we will use $R = 0.08205$ L·atm/mol·K. We can therefore set up

$$T_B = \frac{a}{bR}$$

$$= \frac{0.03508 \; \frac{\text{atm·L}^2}{\text{mol}^2}}{0.0237 \; \frac{\text{L}}{\text{mol}} \cdot 0.08205 \; \frac{\text{L·atm}}{\text{mol·K}}}$$

All of the liter units cancel, as well as the mole units. The atmosphere units also cancel, leaving the unit of K (kelvins) in a denominator of the denominator, which makes it in the numerator. The final answer therefore has units of K, which is what is expected for a temperature. Numerically, we evaluate the fraction and find that

$$T_B = 18.0 \text{ K}$$

Experimentally, it is 25 K.

b. A similar procedure for methane, using a = 2.253 atm·L^2/mol^2 and b = 0.0428 L/mol, yields

$$\frac{2.253 \; \frac{\text{atm·L}^2}{\text{mol}^2}}{0.0428 \; \frac{\text{L}}{\text{mol}} \cdot 0.08205 \; \frac{\text{L·atm}}{\text{mol·K}}} = 641 \text{ K}$$

The experimental value is 509 K.

The fact that the predicted Boyle temperatures are a bit off from the experimental values should not be cause for alarm. Some approximations were made in trying to find a correspondence between the virial equation of state and the van der Waals equation of state. However, equation 1.23 does a good job of estimating the temperature at which a gas will act more like an ideal gas than at others.

We can also use these new equations of state, like the van der Waals equation of state, to derive how certain state variables vary as others are changed. For example, recall that we used the ideal gas law to determine that

$$\left(\frac{\partial p}{\partial T}\right)_{V,n} = \frac{nR}{V}$$

Suppose we use the van der Waals equation of state to determine how pressure varies with respect to temperature, assuming volume and amount are constant. First, we need to rewrite the van der Waals equation so that pressure is all by itself on one side of the equation:

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$p + \frac{an^2}{V^2} = \frac{nRT}{V - nb}$$

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

Next, we take the derivative of this expression with respect to temperature. Note that the second term on the right does not have temperature as a variable, so the derivative of it with respect to T is zero. We get

$$\left(\frac{\partial p}{\partial T}\right)_{V,n} = \frac{nR}{V - nb}$$

We can also determine the volume derivative of pressure at constant temperature and amount

$$\left(\frac{\partial p}{\partial V}\right)_{T,n} = -\frac{nRT}{(V - nb)^2} + \frac{2an^2}{V^3}$$

Both terms on the right side survive this differentiation. Compare this to the equivalent expression from the ideal gas law. Although it is a little more complicated, it agrees better with experimental results for most gases. The derivations of equations of state are usually a balance between simplicity and applicability. Very simple equations of state are often inaccurate for many real situations, but to accurately describe the behavior of a real gas often requires complicated expressions with many parameters. An extreme example is cited in the classic text by Lewis and Randall (*Thermodynamics*, 2nd ed., revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, 1961) as

$$p = RTd + \left(B_0RT - A_0 - \frac{C_0}{T}\right)d^2 + (bRT - a)d^3 + a\alpha d^6 + \frac{cd^2}{T^2}(1 + \gamma d^2)e^{-\gamma d^2}$$

where d is the density and A_0, B_0, C_0, a, b, c, α, and γ are experimentally determined parameters. (This equation of state is applicable to gases cooled or pressurized to near the liquid state.) "The equation . . . yields reasonable agreement, but it is so complex as to discourage its general use." Maybe not in this age of computers, but this equation of state is daunting, nonetheless.

The state variables of a gas can be represented diagrammatically. Figure 1.10 shows an example of this sort of representation, determined from the equation of state.

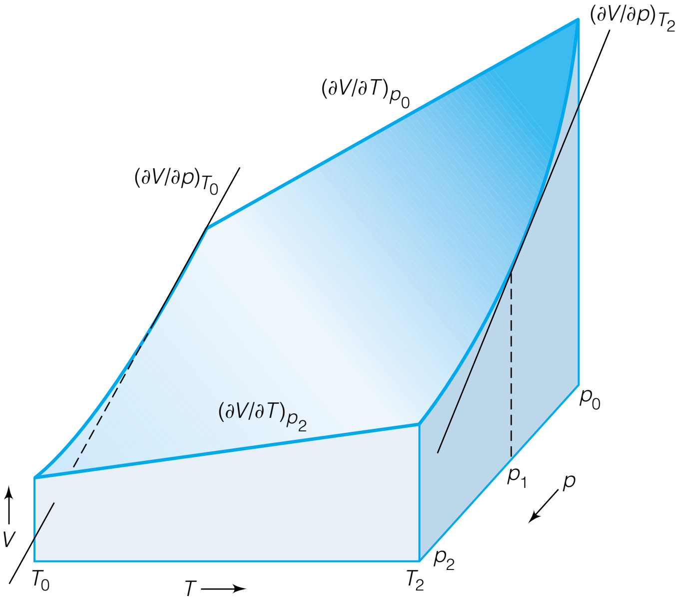


Figure 1.10 The surface that is plotted represents the combination of p, V, and T values that are allowed for an ideal gas according to the ideal gas law. The slope in each dimension represents a different partial derivative. (Adapted with permission from G. K. Vemulapalli, *Physical Chemistry,* Prentice-Hall, Upper Saddle River, N.J., 1993.)

1.7 More on Derivatives

The above examples of taking partial derivatives of equations of state are relatively straightforward. Thermodynamics, however, is well known for using such techniques extensively. We therefore devote this section to a discussion of partial derivative techniques that we will use in the future. The expressions that we derive in thermodynamics using partial derivation can be extremely useful: the behavior of a system that cannot be measured directly can instead be calculated through some of the expressions we derive.

Various rules about partial derivatives are expressed using the general variables A, B, C, D, . . . instead of variables we know. It will be our job to apply these expressions to the state variables of interest. The two rules of particular interest are the chain rule for partial derivatives and the cyclic rule for partial derivatives.

First, you should recognize that a partial derivative obeys some of the same algebraic rules as fractions. For example, since we have determined that

$$\left(\frac{\partial p}{\partial T}\right)_{V,n} = \frac{nR}{V}$$

we can take the reciprocal of both sides to find that

$$\left(\frac{\partial T}{\partial p}\right)_{V,n} = \frac{V}{nR}$$

Note that the variables that remain constant in the partial derivative stay the same in the conversion. Partial derivatives also multiply through algebraically just like fractions, as the following example demonstrates.

If A is a function of two variables B and C, written as $A(B, C)$, and both variables B and C are functions of the variables D and E, written respectively as $B(D, E)$ and $C(D, E)$, then the *chain rule for partial derivatives** is

$$\left(\frac{\partial A}{\partial B}\right)_C = \left(\frac{\partial A}{\partial D}\right)_E\left(\frac{\partial D}{\partial B}\right)_C + \left(\frac{\partial A}{\partial E}\right)_D\left(\frac{\partial E}{\partial B}\right)_C \qquad \mathbf{(1.24)}$$

This makes intuitive sense in that you can cancel ∂D in the first term and ∂E in the second term, if the variable held constant is the same for both partials in each term. This chain rule is reminiscent of the definition of the total derivative for a function of many variables.

In the cases of p, V, and T, we can use equation 1.24 to develop the *cyclic rule*. For a given amount of gas, pressure depends on V and T, volume depends on p and T, and temperature depends on p and V. For any general state variable of a gas F, its total derivative (which is ultimately based on equation 1.12) with respect to temperature at constant p would be

$$\left(\frac{\partial F}{\partial T}\right)_p = \left(\frac{\partial F}{\partial T}\right)_V\left(\frac{\partial T}{\partial T}\right)_p + \left(\frac{\partial F}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p$$

The term $(\partial T/\partial T)_p$ is simply 1, since the derivative of a variable with respect to itself is always 1. If F is the pressure p, then $(\partial F/\partial T)_p = (\partial p/\partial T)_p = 0$, since p is held constant. The above expression becomes

$$0 = \left(\frac{\partial p}{\partial T}\right)_V + \left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p$$

---

*We present the chain rule here, but do not derive it. Derivations can be found in most calculus books.

We can rearrange this. Bringing one term to the other side of the equation, we get

$$\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p$$

Multiplying everything to one side yields

$$\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial T}{\partial V}\right)_p = -1 \tag{1.25}$$

This is the cyclic rule for partial derivatives. Notice that each term involves p, V, and T. This expression is independent of the equation of state. Knowing any two derivatives, one can use equation 1.25 to determine the third, no matter what the equation of state of the gaseous system is.

The cyclic rule is sometimes rewritten in a different form that may be easier to remember, by bringing two of the three terms to one side of the equation and expressing the equality in fractional form by taking the reciprocal of one partial derivative. One way to write it would be

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} \tag{1.26}$$

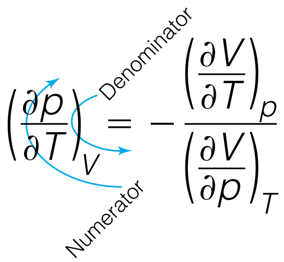


Figure 1.11 A mnemonic for remembering the fraction form of the cyclic rule. The arrows show the ordering of the variables in each partial derivative in the numerator and denominator. The only other thing to remember to include in the expression is the negative sign.

This might look more complicated, but consider the mnemonic in Figure 1.11. There is a systematic way of constructing the fractional form of the cyclic rule that might be useful. The mnemonic in Figure 1.11 works for any partial derivative in terms of p, V, and T.

Example 1.7

Given the expression

$$\left(\frac{\partial p}{\partial T}\right)_{V,n} = -\left(\frac{\partial p}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{p,n}$$

determine an expression for

$$\left(\frac{\partial V}{\partial p}\right)_{T,n}$$

Solution

There is an expression involving V and p at constant T and n on the right side of the equality, but it is written as the reciprocal of the desired expression. First, we can take the reciprocal of the entire expression to get

$$\left(\frac{\partial T}{\partial p}\right)_{V,n} = -\left(\frac{\partial V}{\partial p}\right)_{T,n}\left(\frac{\partial T}{\partial V}\right)_{p,n}$$

Next, in order to solve for $(\partial V/\partial p)_{T,n}$, we can bring the other partial derivative to the other side of the equation, using the normal rules of algebra for fractions. Moving the negative sign as well, we get

$$-\left(\frac{\partial T}{\partial p}\right)_{V,n}\left(\frac{\partial V}{\partial T}\right)_{p,n} = \left(\frac{\partial V}{\partial p}\right)_{T,n}$$

which provides us with the necessary expression.

Example 1.8

Use the cyclic rule to determine an alternate expression for

$$\left(\frac{\partial V}{\partial P}\right)_T$$

Solution

Using Figure 1.11, it should be easy to see that

$$\left(\frac{\partial V}{\partial p}\right)_T = -\frac{\left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{\partial T}{\partial V}\right)_p}$$

You should verify that this is correct.

1.8 A Few Partial Derivatives Defined

Many times, gaseous systems are used to introduce thermodynamic concepts. That's because generally speaking, gaseous systems are well behaved. That is, we have a good idea how they will change their state variables when a certain state variable, controlled by us, is changed. Therefore gaseous systems are an important part of our initial understanding of thermodynamics.

It is useful to define a few special partial derivatives in terms of the state variables of gaseous systems, because the definitions either (a) can be considered as basic properties of the gas, or (b) will help simplify future equations.

The *expansion coefficient* of a gas, labeled α, is defined as the change in volume as the temperature is varied at constant pressure. A $1/V$ multiplicative factor is included:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{1.27}$$

For an ideal gas, it is easy to show that $\alpha = R/pV$.

The *isothermal compressibility* of a gas, labeled κ, is the change in volume as the pressure changes at constant temperature (the name of this coefficient is more descriptive). It too has a $1/V$ multiplicative factor, but it is negative:

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{1.28}$$

Because $(\partial V/\partial p)_T$ is negative for gases, the minus sign in equation 1.28 makes κ a positive number. Again for an ideal gas, it is easy to show that $\kappa = RT/p^2V$. For both α and κ, the $1/V$ term is included to make the quantities intensive (that is, independent of amount*).

Since both of these definitions use p, V, and T, we can use the cyclic rule to show that, for example,

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa}$$

---

*Recall that intensive properties (like temperature and density) are independent of amount of material, whereas extensive properties (like mass and volume) are dependent on the amount of material.

Such relationships are particularly useful for systems where, for example, it might be impossible to keep the volume of the system constant. The constant-volume derivative can be expressed in terms of derivatives at constant temperature and constant pressure, two conditions that are easy to control in any laboratory setting.

1.9 Summary

Gases are introduced first in a detailed study of thermodynamics because their behavior is simple. Boyle enunciated his gas law about the relationship between pressure and volume in 1662, making it one of the oldest of modern chemical principles. Although it is certain that not all of the "simple" ideas have been discovered, in the history of science the more straightforward ideas were developed first. Because the behavior of gases was so easy to understand, even with more complicated equations of state, they became the systems of choice for studying other state variables. Also, the calculus tool of partial derivatives is easy to apply to the behavior of gases. As such, a discussion of the properties of gases is a fitting introductory topic for the subject of thermodynamics. A desire to understand the state of a system of interest, which includes state variables not yet introduced and uses some of the tools of calculus, is at the heart of thermodynamics. We will proceed to develop such an understanding in the next seven chapters.

1.2 System, Surroundings, and State

1.1. A bomb calorimeter is a sturdy metal vessel in which samples can be ignited and the amount of heat given off can be measured as the heat warms up surrounding water. Draw a rough sketch of such an experimental setup and label **(a)** the system and **(b)** the surroundings.

1.2. Differentiate between a system and a closed system. Give examples of both.

1.3. Use the equalities listed in Table 1.1 to convert the given values to the desired units. **(a)** 12.56 L to cm^3 **(b)** 45°C to K **(c)** 1.055 atm to Pa **(d)** 1233 mmHg to bar **(e)** 125 mL to cubic centimeters **(f)** 4.2 K to °C **(g)** 25,750 Pa to bar

1.4. Which temperature is higher? **(a)** 0 K or 0°C **(b)** 300 K or 0°C **(c)** 250 K or −20°C

1.3 & 1.4 Zeroth Law of Thermodynamics; Equations of State

1.5. A pot of cold water is heated on a stove, and when the water boils a fresh egg is placed in the water to cook. Describe the events that are occurring in terms of the zeroth law of thermodynamics.

1.6. What is the value of $F(T)$ for a sample of gas whose volume is 2.97 L and pressure is 0.0553 atm? What would the volume of the gas be if the pressure were increased to 1.00 atm?

1.7. What is the value of $F(p)$ for a sample of gas whose temperature is −33.0°C and volume is 0.0250 L? What temperature is required to change the volume to 66.9 cm^3?

1.8. Calculate the value of the constant in equation 1.9 for a 1.887-mol gas sample with a pressure of 2.66 bar, a volume of 27.5 L, and a temperature of 466.9 K. Compare your answer to the values in Table 1.2. Are you surprised with your answer?

1.9. Show that one value of R, with its associated units, equals another value of R with its different associated units.

1.10. Use the two appropriate values of R to determine a conversion between L·atm and J.

1.11. Calculations using STP and SATP use (the same? different?) value(s) of R. Choose one phrase to make the statement correct and defend your choice.

1.5 More on Ideal Gases

1.12. Pressures of gases in mixtures are referred to as *partial pressures* and are additive. 1.00 L of He gas at 0.75 atm is mixed with 2.00 L of Ne gas at 1.5 atm at a temperature of 25.0°C to make a total volume of 3.00 L of a mixture. Assuming no temperature change and that He and Ne can be approximated as ideal gases, what are **(a)** the total resulting pressure, **(b)** the partial pressures of each component, and **(c)** the mole fractions of each gas in the mix?

1.13. Earth's atmosphere is approximately 80% N_2 and 20% O_2. If the total atmospheric pressure at sea level is about 14.7 lb/in.^{2} (where lb/in.^{2} is pounds per square inch, a common but non-SI unit of pressure), what are the partial pressures of N_2 and O_2 in units of lbs/in.^{2}?

1.14. The atmospheric surface pressure on Venus is 90 bar and is composed of 96% carbon dioxide and approximately 4% various other gases. Given a surface temperature of 730 K, what is the mass of carbon dioxide present per cubic centimeter at the surface?

1.15. What are the slopes of the following lines at the point $x = 5$? at $x = 10$? **(a)** $y = 5x + 7$ **(b)** $y = 3x^2 - 5x + 2$ **(c)** $y = 7/x$.

1.16. For the following function, evaluate the derivatives in a–f below.

$$F(w, x, y, z) = 3xy^2 + \frac{w^3z^3}{32y} - \frac{xy^2z^3}{w}$$

(a) $\left(\frac{\partial F}{\partial x}\right)_{w,y,z}$

(b) $\left(\frac{\partial F}{\partial w}\right)_{w,y,z}$

(c) $\left(\frac{\partial F}{\partial y}\right)_{w,y,z}$

(d) $\left[\frac{\partial}{\partial z}\left(\frac{\partial F}{\partial x}\right)_{w,y,z}\right]_{w,x,y}$

(e) $\left[\frac{\partial}{\partial x}\left(\frac{\partial F}{\partial z}\right)_{w,x,y}\right]_{w,y,z}$

(f) $\left\{\frac{\partial}{\partial w}\left[\frac{\partial}{\partial z}\left(\frac{\partial F}{\partial x}\right)_{w,y,z}\right]_{w,x,y}\right\}_{x,y,z}$

1.17. Determine the expressions for the following expressions, assuming that the ideal gas law holds.

(a) $\left(\frac{\partial V}{\partial p}\right)_{T,n}$

(b) $\left(\frac{\partial V}{\partial n}\right)_{T,p}$

(c) $\left(\frac{\partial T}{\partial V}\right)_{n,p}$

(d) $\left(\frac{\partial p}{\partial T}\right)_{n,V}$

(e) $\left(\frac{\partial p}{\partial n}\right)_{T,V}$

1.18. Why do you think that none of the above exercises ask you to take a derivative with respect to R? Is it the same reason that we do not define the derivative of R with respect to any other variable?

1.19. When a given amount of air is let out of an automobile tire, it changes its volume and pressure simultaneously, and as a result of this the temperature of the air changes. Write a derivative that stands for this change. (*Hint:* it will be a double derivative as in 1.16e above.)

1.6 Real Gases

1.20. Liquid nitrogen comes in large cylinders that require special tank carts and hold 120 L of liquid at 77 K. Given the density of liquid nitrogen of 0.840 g/cm^3, use the van der Waals equation to estimate the volume of the nitrogen gas after it evaporates at 77 K. (*Hint:* because V shows up in two places in the van der Waals equation, you will have to do an iteration procedure to estimate V. Neglect the an^2/V^2 term initially and calculate V; then substitute this into the an^2/V^2 term, evaluate the pressure term, resolve for V, and repeat until the number doesn't change. A programmable calculator or spreadsheet program might be useful.)

1.21. Calculate the Boyle temperatures for carbon dioxide, oxygen, and nitrogen using the van der Waals constants in Table 1.6. How close do they come to the experimental values from Table 1.5?

1.22. Determine the expression for $(\partial p/\partial V)_T$ for a van der Waals gas and for the virial equation in terms of volume.

1.23. What are the units of the virial coefficient C? of C'?

1.24. Table 1.4 shows that the second virial coefficient B for He is negative at low temperature, seems to maximize at a little over 12.0 cm^3/mol, and then decreases. Do you think it will become negative again at higher temperatures? Why is it decreasing?

1.25. Use Table 1.5 to list the gases from most ideal to least ideal. What trend or trends are obvious from this list?

1.26. What is the van der Waals constant a for Ne in units of bar·cm^6/mol^2?

1.27. By definition, the compressibility of an ideal gas is 1. By approximately what percentage does this change for hydrogen upon inclusion of the second virial coefficient term? How about for water vapor? Give the conditions under which you make this estimate.

1.28. The second virial coefficient B and the third virial coefficient C for Ar are -0.021 L/mol and 0.0012 L^2/mol^2 at 273 K, respectively. By what percentage does the compressibility change when you include the third virial term?

1.29. Use the approximation $(1 - x)^{-1} \approx 1 + x + x^2 + \cdots$ to determine an expression for C in terms of the van der Waals constants.

1.30. Why is nitrogen a good choice for the study of ideal gas behavior around room temperature?

1.7 & 1.8 Partial Derivatives and Definitions

1.31. Write two other forms of the cyclic rule in equation 1.26, using the mnemonic in Figure 1.11.

1.32. Use Figure 1.11 to construct the cyclic rule equivalent of $(\partial p/\partial p)_T$. Does the answer make sense in light of the original partial derivative?

1.33. What are the units for α and κ?

1.34. Why is it difficult to determine an analytic expression for α and κ for a van der Waals gas?

1.35. Show that $\kappa = (T/p)\alpha$ for an ideal gas.

1.36. Determine an expression for $(\partial V/\partial T)_{p,n}$ in terms of α and κ. Does the sign on the expression make sense in terms of what you know happens to volume as temperature changes?

1.37. Density is defined as molar mass, M, divided by molar volume:

$$d = \frac{M}{\overline{V}}$$

Evaluate $(\partial d/\partial T)_{p,n}$ for an ideal gas in terms of M, $\overline{V}$, and p.

1.38. Write the fraction α/κ in a different form using the cyclic rule of partial derivatives.

Symbolic Math Exercises

(Note: The Symbolic Math Exercise problems at the end of each chapter are more complex, and typically require additional tools like a symbolic math program—MathCad, Maple, Mathematica—or a programmable calculator.)

1.39. Table 1.4 gives different values of the second virial coefficient B for different temperatures. Assuming standard pressure of 1 bar, determine the molar volumes of He, Ne, and Ar for the different temperatures. What does a graph of V versus T look like?

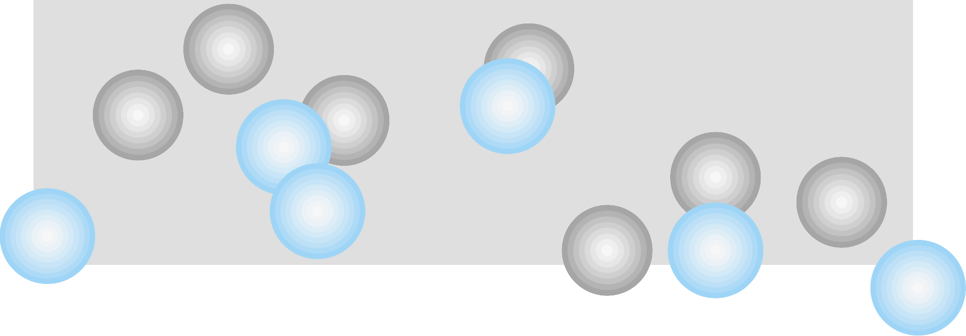
1.40. Using the van der Waals constants given in Table 1.6, predict the molar volumes of **(a)** krypton, Kr; **(b)** ethane, C_2H_6; and **(c)** mercury, Hg, at 25°C and 1 bar pressure.

1.41. Use the ideal gas law to symbolically prove the cyclic rule of partial derivatives.

1.42. Using your results from exercise 1.39, can you set up the expressions to evaluate α and κ for Ar?

2

The First Law of Thermodynamics



THE PREVIOUS CHAPTER ESTABLISHED THAT MATTER BEHAVES ACCORDING TO CERTAIN RULES called equations of state. We can now begin to understand the rules by which *energy* behaves. Even though we will primarily be using gases as examples, the ideas of thermodynamics are applicable to all systems, whether solid, liquid, gas, or any combination of phases.

Thermodynamics was developed mostly in the nineteenth century. This was after the acceptance of the modern atomic theory of Dalton but before the ideas of quantum mechanics (which imply that the microscopic universe of atoms and electrons follow different rules than the macroscopic world of large masses). Therefore, thermodynamics mostly deals with large collections of atoms and molecules. The laws of thermodynamics are *macroscopic* rules. Later in the text we will cover *microscopic* rules (that is, quantum mechanics), but for now remember that thermodynamics deals with systems we can see, feel, weigh, and manipulate with our own hands.

2.1 Synopsis

First, we will define work, heat, and internal energy. The first law of thermodynamics is based on the relationship between these three quantities. Internal energy is one example of a state function. State functions have certain properties that we will find useful. Another state function, enthalpy, will also be introduced. Changes in state functions will be considered, and we will develop ways to calculate how internal energy and enthalpy change during a physical or chemical process. We will also introduce heat capacities and Joule-Thomson coefficients, both of which are related to temperature changes in systems. We will end the chapter by recognizing that the first law of thermodynamics is limited in its predictions, and that other ideas—other laws of thermodynamics—are needed to understand how energy interacts with matter.

2.2 Work and Heat

Physically, *work* is performed on an object when the object moves some distance s due to the application of a force F. Mathematically, it is the dot product of the force vector $\mathbf{F}$ and the distance vector $\mathbf{s}$:

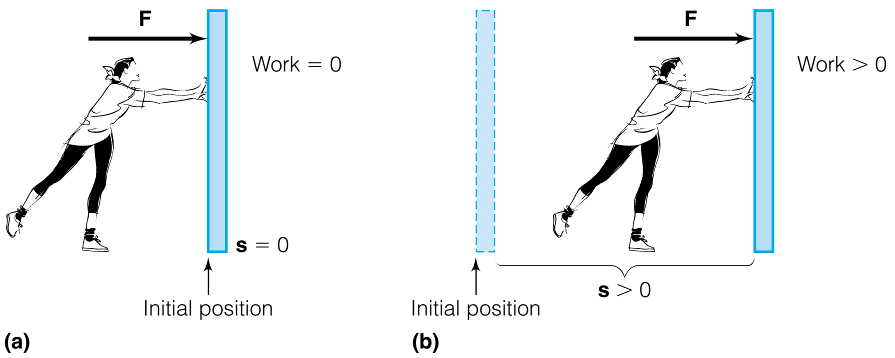


Figure 2.1 When a force is exerted on an object, no work is done unless the object moves. (a) Since the wall does not move, no work is done. (b) Work is done because the force is acting through a distance.

$$\text{work} = \mathbf{F} \cdot \mathbf{s} = |F|\,|s| \cos \theta \tag{2.1}$$

where θ is the angle between the vectors. Work is a scalar, not vector, quantity. Work has magnitude, but not direction. Figure 2.1 shows a force acting on an object. In Figure 2.1a, the object is not moving, so the amount of work is zero (despite the amount of force being exerted). In Figure 2.1b, an object has been moved, so work was done.

Work has units of joules, like energy. This is not without a reason: work is a way to transfer energy. Energy is defined as the ability to do work, so it makes sense that energy and work are described using the same units.

The most common form of work studied by basic thermodynamics involves the changing volume of a system. Consider Figure 2.2a. A frictionless piston confines a sample of a gas in an initial volume V_i. The gas inside the chamber also has an initial pressure p_i. Initially, what keeps the piston at a fixed position is the external pressure of the surroundings, p_ext.

If the piston moves out, Figure 2.2b, then the *system is doing work* on the surroundings. That means that the system is *losing* energy in the form of work. The infinitesimal amount of work dw that the system does on the surroundings for an infinitesimal change in volume dV while acting against a constant external pressure p_ext is defined as

$$dw = -p_\mathrm{ext}\, dV \tag{2.2}$$

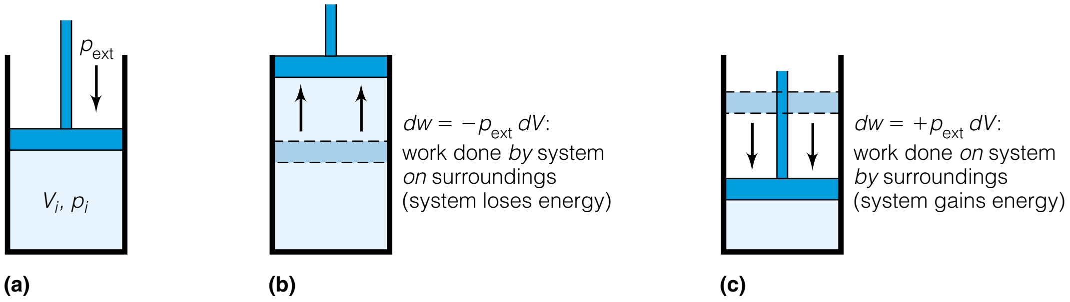


Figure 2.2 (a) A frictionless piston with an enclosed gas is a simple example of how gases perform work on systems or surroundings. (b) The work is done on the surroundings. (c) The work is done on the system. The mathematical definition of work remains the same, however.

The negative sign indicates that the work done contributes to a *decrease* in the amount of energy of the system.* If the piston moves inward, Figure 2.2c, then the surroundings are doing work *on the system,* and the amount of energy in the system is increased. The infinitesimal amount of work done on the system is defined by equation 2.2, but because the volume change dV is in the opposite direction, the work now has a positive value. Notice that our focus is the system. The work is positive or negative with respect to the system, which is the part of the universe of interest to us.

If we add up all of the (infinite) infinitesimal changes that contribute to an overall change, we get the total amount of work done on or by the system. Calculus uses the integral to add up infinitesimal changes. The total amount of work, w, for a change as represented in Figure 2.2 is therefore

$$w = -\int p_{\text{ext}}\, dV \tag{2.3}$$

Whether this integral can be simplified or not depends on the conditions of the process. If the external pressure remains constant throughout the process, then it can be removed to outside the integral and the expression becomes

$$w = -\int p_{\text{ext}}\, dV = -p_{\text{ext}} \int dV = -p_{\text{ext}} \cdot V\Big|_{V_{\text{i}}}^{V_{\text{f}}}$$

In this case, the limits on the integral are the initial volume, V_{i}, and the final volume, V_{f}, of the process. This is reflected in the last expression in the equation above. Evaluating the integral at its limits, we get

$$w = -p_{\text{ext}}(V_{\text{f}} - V_{\text{i}})$$

$$w = -p_{\text{ext}} \cdot \Delta V \tag{2.4}$$

If the external pressure is not constant throughout the process, then we will need some other way of evaluating the work in equation 2.3.

By using pressures in units of atm and volumes in units of L, we get a unit of work in L·atm. This is not a common work unit. The SI unit for work is the joule, J. However, using the various values of R from the previous chapter, it can be shown that 1 L·atm = 101.32 J. This conversion factor is very useful to get work into its proper SI units. If volume were expressed in units of m^3 and pressure in pascals, units of joules would be obtained directly since

$$\text{Pa} \times \text{m}^3 = \frac{\text{N}}{\text{m}^2} \times \text{m}^3 = \text{N} \times \text{m} = \text{J}$$

Example 2.1

Consider an ideal gas in a piston chamber, as in Figure 2.2, where the initial volume is 2.00 L and the initial pressure is 8.00 atm. Assume that the piston is moving up (that is, the system is expanding) to a final volume of 5.50 L against a constant external pressure of 1.75 atm. Also assume constant temperature for the process.

a. Calculate the work for the process.
b. Calculate the final pressure of the gas.

---

*It is easy to show that the two definitions of work are equivalent. Since pressure is force per unit area, equation 2.2 can be rewritten as work = $\frac{\text{force}}{\text{area}}$ × volume = force × distance, which is equation 2.1.

Solution

a. First, the change in volume is needed. We find it as follows:

$$\Delta V = V_f - V_i = 5.50 \text{ L} - 2.00 \text{ L} = 3.50 \text{ L}$$

To calculate the work against the constant external pressure, we use equation 2.4:

$$w = -p_{ext}\,\Delta V = -(1.75 \text{ atm})(3.50 \text{ L}) = -6.13 \text{ L·atm}$$

If we want to convert units to the SI units of joules, we use the appropriate conversion factor:

$$-6.13 \text{ L·atm} \times \frac{101.32 \text{ J}}{\text{L·atm}} = -621 \text{ J}$$

That is, 621 joules have been lost by the system during the expansion.

b. Because of the assumption of an ideal gas, we can use Boyle's law to calculate the final gas pressure. We get

$$(2.00 \text{ L})(8.00 \text{ atm}) = (5.50 \text{ L})(p_f)$$

$$p_f = 2.91 \text{ atm}$$

Figure 2.3 illustrates a condition that occasionally occurs with gases: the expansion of a gas into a larger volume which is initially a vacuum. In such a case, since the gas is expanding against a p_{ext} of 0, by the definition of work in equation 2.4 the work done by the gas equals zero. Such a process is called a *free expansion:*

$$\text{work} = 0 \text{ for free expansion} \tag{2.5}$$

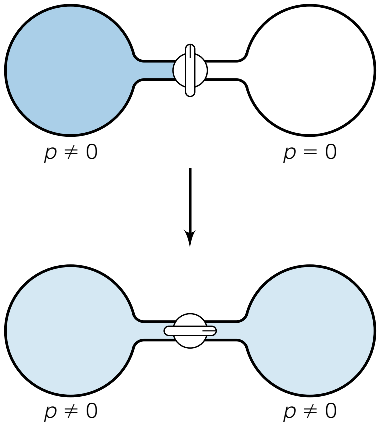


Figure 2.3 No work is performed if a sample of gas expands into a vacuum.

Example 2.2

From the conditions and the given definitions of the system, determine whether there is work done by the system, work done on the system, or no work done.

a. A balloon expands as a small piece of dry ice (solid CO_2) inside the balloon sublimes (balloon = system).

b. The space shuttle's cargo bay doors are opened to space, releasing a little bit of residual atmosphere (cargo bay = system).

c. Gaseous CHF_2Cl, a refrigerant, is compressed in the compressor of an air conditioner, to try to liquefy it (CHF_2Cl = system).

d. A can of spray paint is discharged (can = system).

e. Same as part d, but consider the spray to be the system.

Solution

a. Since the balloon is increasing in volume, it is undoubtedly doing work: work is done by the system.

b. When the shuttle's cargo bay doors are opened in space, the bay is being opened to vacuum (although not a perfect one), so we are considering relatively free expansion. Therefore no work is done.

c. When CHF_2Cl is compressed, its volume is decreased, so work is being done on the system.

d, e. When a can of spray paint is discharged, the can itself usually does not change in volume. Therefore, if the can itself is defined as the system, the amount of work it does is zero. However, work is done by the spray itself as it expands against the atmosphere. This last example shows how important it is to define the system as specifically as possible.

If it were possible, we could change the volume of the gas inside the piston chamber in infinitesimally small steps, allowing the system to react to each infinitesimal change before making the next change. At each step, the system comes to equilibrium with its surroundings so that the entire process is one of a continuous equilibrium state. (In reality, that would require an infinite number of steps for any finite change in volume. Sufficiently slow changes are a good approximation.) Such a process is called *reversible.* Processes that are not performed this way (or are not approximated this way) are called *irreversible.* Many thermodynamic ideas are based on systems that undergo reversible processes. Volume changes aren't the only processes that can be reversible. Thermal changes, mechanical changes (that is, moving a piece of matter), and other changes can be modeled as reversible or irreversible.

Gaseous systems are useful examples for thermodynamics because we can use various gas laws to help us calculate the amount of pressure-volume work when a system changes volume. This is especially so for reversible changes, because most reversible changes occur by letting the external pressure equal the internal pressure:

$$p_{\text{ext}} = p_{\text{int}} \text{ for reversible change}$$

The following substitution can then be made for reversible changes:

$$w_{\text{rev}} = -\int p_{\text{int}}\, dV \qquad \textbf{(2.6)}$$

So now we can determine the work for a process in terms of the *internal* pressure.

The ideal gas law can be used to substitute for the internal pressure, because if the system is composed of an ideal gas, the ideal gas law must hold. We can get

$$w_{\text{rev}} = -\int \frac{nRT}{V} dV$$

when we substitute for pressure. Although n and R are constants, the temperature T is a variable and may change. However, if the temperature does remain constant for the process, the term *isothermal* is used to describe the process, and the temperature "variable" can be taken outside of the integral sign. Volume remains inside the integral because it is the variable being integrated. We get

$$w_{\text{rev}} = -nRT \int \frac{1}{V}\, dV$$

This integral has a standard form; we can evaluate it. The equation becomes

$$w_{\text{rev}} = -nRT \left(\ln V\big|_{V_{\text{i}}}^{V_{\text{f}}}\right)$$

The "ln" refers to the natural logarithm, not the base 10 logarithm (which is represented by "log"). Evaluating the integral at its limits,

$$w_{\text{rev}} = -nRT\,(\ln V_{\text{f}} - \ln V_{\text{i}})$$

which, using the properties of logarithms, is

$$w_{\text{rev}} = -nRT \ln \frac{V_f}{V_i} \tag{2.7}$$

for an isothermal, reversible change in the conditions of an ideal gas. Using Boyle's law for gas, we can substitute the expression p_i/p_f for the volumes in the logarithm and also see that

$$w_{\text{rev}} = -nRT \ln \frac{p_i}{p_f} \tag{2.8}$$

for an ideal gas undergoing an isothermal process.

Example 2.3

Gas in a piston chamber kept in a constant-temperature bath at 25.0°C expands from 25.0 mL to 75.0 mL very, very slowly, as illustrated in Figure 2.4. If there is 0.00100 mole of ideal gas in the chamber, calculate the work done by the system.

Solution

Since the system is kept in a constant-temperature bath, the change is an isothermal one. Also, since the change is very, very slow, we can presume that the change is reversible. Therefore we can use equation 2.7. We find

$$w_{\text{rev}} = -(0.00100 \text{ mol})\left(8.314 \frac{\text{J}}{\text{mol·K}}\right)(298.15 \text{ K})\left(\ln \frac{75.0 \text{ mL}}{25.0 \text{ mL}}\right)$$

$$w_{\text{rev}} = -2.72 \text{ J}$$

That is, 2.72 J is lost by the system.

Heat, symbolized by the letter q, is more difficult to define than work. Heat is a measure of thermal energy transfer that can be determined by the change in the temperature of an object. That is, heat is a way of following a *change* in energy of a system. Because heat is a change in energy, we use the same units for heat as we do for energy: joules.

Even historically, heat was a difficult concept. It used to be thought that heat was a property of a system that could be isolated and bottled as a substance in

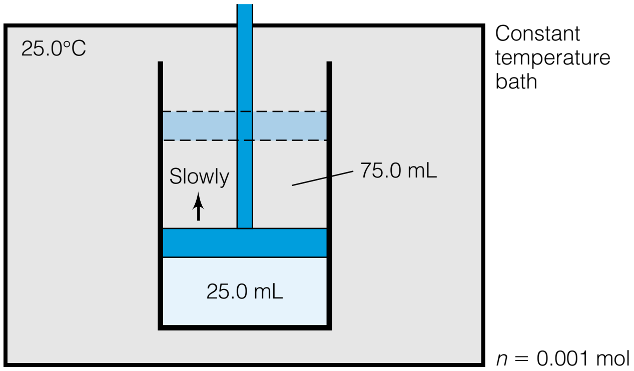


Figure 2.4 A piston chamber in a constant-temperature bath, undergoing a reversible change in volume. See Example 2.3.


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Figure 2.5 James Prescott Joule (1818–1889), English physicist. His work established the interconversion of heat and work as forms of energy, and laid the foundation for the first law of thermodynamics.

its own right. This substance was even given a name: "caloric." However, around 1780 Benjamin Thompson, later Count Rumford, kept track of the production of heat during the boring of cannon barrels and concluded that the amount of heat was related to the amount of work done in the process. In the 1840s, careful experiments by the English physicist James Prescott Joule (Figure 2.5) verified this. A brewer at the time, Joule used an apparatus like the one shown in Figure 2.6 to perform the work of mixing a quantity of water using a weight on a pulley. By making careful measurements of the temperature of the water and of the work being performed by the falling weight (using equation 2.1), Joule was able to support the idea that work and heat were manifestations of the same thing. (In fact, the phrase "mechanical equivalent of heat" is still used occasionally and emphasizes their relationship.) The SI unit of energy and work and heat, the joule, is named in Joule's honor.

The older unit of energy and heat and work, the calorie, is defined as the amount of heat needed to raise the temperature of exactly 1 mL of water by 1°C from 15°C to 16°C. The relationship between the calorie and the joule is

$$1 \text{ calorie} = 4.184 \text{ joules} \tag{2.8}$$

Although joules are the accepted SI unit, the unit of calorie is still used often, especially in the United States.

Heat can go into a system, so that the temperature of the system increases, or it can come out of a system, in which case the temperature of the system decreases. For any change where heat goes into a system, q is positive. On the


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Figure 2.6 Joule used this apparatus to measure what was once called the "mechanical equivalent of heat."

other hand, if heat comes out of a system, q is negative. The sign on q therefore tells one the direction of the heat transfer.

The same change in temperature requires a different amount of heat for different materials. For example, a system composed of 10 cm^3 of iron metal gets hotter with less heat than does 10 cm^3 of water. In fact, the amount of heat necessary to change the temperature is proportional to the magnitude of the temperature change, ΔT, and the mass of the system m:

$$q \propto m \cdot \Delta T$$

In order to convert a proportionality to an equality, a proportionality constant is needed. For the above expression, the proportionality constant is represented by the letter c (sometimes s) and is called the *specific heat* (or *specific heat capacity*):

$$q = m \cdot c \cdot \Delta T \tag{2.9}$$

The specific heat is an intensive characteristic of the material composing the system. Materials with a low specific heat, like many metals, need little heat for a relatively large change in temperature. Table 2.1 lists some specific heats for selected materials. Units for specific heat are (energy)/(mass·temperature) or (energy)/(moles·temperature), so although the SI units for specific heat are J/g·K or J/mol·K, it is not unusual to see specific heats having units of cal/mol·°C or some other set of units. Notice that, because equation 2.9 involves the *change* in temperature, it does not matter if the temperature has units of kelvins or degrees Celsius.

Heat capacity C is an extensive property that includes the amount of material in the system, so equation 2.9 would be written as

$$q = C \cdot \Delta T$$

Table 2.1 Specific heat capacities of various materials

Material	c **(J/g·K)**
Al	0.900
Al_2O_3	1.275
C_2H_5OH, ethanol	2.42
C_6H_6, benzene (vapors)	1.05
C_6H_{14}, *n*-hexane	1.65
Cu	0.385
Fe	0.452
Fe_2O_3	0.651
H_2 (g)	14.304
H_2O (s)	2.06
H_2O (ℓ), 25°C	4.184
H_2O (g), 25°C	1.864
H_2O, steam, 100°C	2.04
Hg	0.138
NaCl	0.864
O_2 (g)	0.918

Example 2.4

a. Assuming that 400. J of energy is put into 7.50 g of iron, what will be the change in temperature? Use $c = 0.450$ J/g·K.

b. If the initial temperature of the iron is 65.0°C, what is the final temperature?

Solution

a. Using equation 2.9:

$$+400.\ \text{J} = (7.50\ \text{g})(0.450\ \text{J/g·K})\Delta T$$

Solving for ΔT:

$$\Delta T = +118\ \text{K}$$

The temperature increases by 118 K, which is equal to a temperature change of 118°C.

b. With an initial temperature of 65.0°C, an increase of 118°C brings the sample to 183°C.

Example 2.5

With reference to Joule's apparatus in Figure 2.6, assume that a 40.0-kg weight (which experiences a force due to gravity of 392 newtons) falls a distance of 2.00 meters. The paddles immersed in the water transfer the decrease in potential energy to the water, which heats up. Assuming a mass of 25.0 kg of water in the vat, what is the expected temperature change of the water? The specific heat of water is 4.18 J/g·K.

Solution

Using equation 2.1, we can calculate the work done on the water by the falling weight:

$$\text{work} = F \cdot s = (392 \text{ N})(2.00 \text{ m}) = 784 \text{ N·m} = 784 \text{ J}$$

where we are using the fact that 1 joule = 1 newton × 1 meter. If all of this work goes into heating the water, we get

$$784 \text{ J} = (25.0 \text{ kg})\left(\frac{1000 \text{ g}}{1 \text{ kg}}\right)(4.18 \text{ J/g·K})\ \Delta T$$

$$\Delta T = 0.00750 \text{ K}$$

This is not a large change in temperature. In fact, Joule had to drop the weight many times before a detectable temperature change was noted.

2.3 Internal Energy and the First Law of Thermodynamics

Work and heat are manifestations of energy, but so far we have not discussed energy directly. That will change here, and from now on energy and energy relationships will be a major focus of our discussion of thermodynamics.

The total energy of a system is defined as the *internal energy,* symbolized as U. The internal energy is composed of energy from different sources, like chemical, electronic, nuclear, and kinetic energies. Because we cannot completely measure all types of energy in any system, the absolute total internal energy of any system cannot be known. But all systems have some total energy U.

An *isolated system* does not allow for passage of matter or energy into or out of the system. (A *closed system,* on the other hand, allows for passage of energy but not matter.) If energy cannot move in or out, then the total energy U of the system does not change. The explicit statement of this is considered the first law of thermodynamics:

The first law of thermodynamics: For an isolated system,
the total energy of the system remains constant.

This does not mean that the system itself is static or unchanging. Something may be occurring in the system, like a chemical reaction or the mixing of two gases. But if the system is isolated, the total energy of the system does not change.

There is a mathematical way of writing the first law, using the internal energy:

$$\text{For an isolated system, } \Delta U = 0 \tag{2.10}$$

For an infinitesimal change, equation 2.10 can be written as $dU = 0$ instead.

The equation 2.10 statement of the first law has limited utility, because in studying systems we usually allow matter or energy to pass to and from the system and the surroundings. In particular, we are interested in energy changes of the system. In all investigations of energy changes in systems, it has been found that when the total energy of a system changes, the energy change goes into either work or heat; nothing else. Mathematically, this is written as

$$\Delta U = q + w \tag{2.11}$$

Equation 2.11 is another way of stating the first law. Note both the simplicity and the importance of this equation. The change in the internal energy for a process is equal to the work plus the heat. Only work or heat (or both) will accompany a change in internal energy. Since we know how to measure work and heat, we can keep track of *changes* in the total energy of a system. The following example illustrates.

Example 2.6

A sample of gas changes in volume from 4.00 L to 6.00 L against an external pressure of 1.50 atm, and simultaneously absorbs 1000 J of heat. What is the change in the internal energy of the system?

Solution

Since the system is absorbing heat, the energy of the system is being increased and so we can write that $q = +1000$ J. Using equation 2.4 for work:

$$w = -p_{\text{ext}}\,\Delta V = -(1.50\text{ atm})(6.00\text{ L} - 4.00\text{ L})$$

$$w = -(1.50\text{ atm})(2.00\text{ L}) = -3.00\text{ L}\cdot\text{atm} \times \frac{101.32\text{ J}}{\text{L}\cdot\text{atm}}$$

$$w = -304\text{ J}$$

The change in internal energy is the sum of w and q:

$$\Delta U = q + w = 1000\text{ J} - 304\text{ J}$$

$$\Delta U = 696\text{ J}$$

Note that q and w have opposite signs, and that the overall change in internal energy is positive. Therefore, the total energy of our gaseous system increases.

If a system is insulated well enough, heat will not be able to get into the system or leave the system. In this situation, $q = 0$. Such systems are called *adiabatic*. For adiabatic processes,

$$\Delta U = w \tag{2.12}$$

This restriction, that $q = 0$, is the first of many restrictions that simplify the thermodynamic treatment of a process. It will be necessary to keep track of these restrictions, because many expressions like equation 2.12 are useful only when such restrictions are applied.

2.4 State Functions

Have you noticed that we use lowercase letters to represent things like work and heat but a capital letter for internal energy? There is a reason for that. Internal energy is an example of a state function, whereas work and heat are not.

A useful property of state functions will be introduced with the following analogy. Consider the mountain in Figure 2.7. If you are a mountain climber

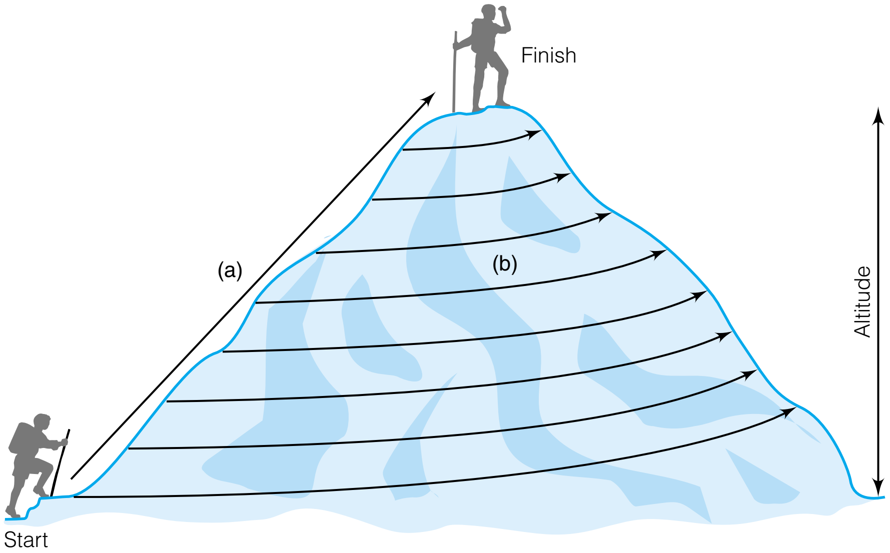

Figure 2.7 Analogy for the definition of a state function. For both path (a) straight up a mountain and path (b) spiraling up the mountain, the overall change in altitude is the same and so is path-independent: the change in altitude is a state function. However, the overall length of the path is path-dependent, and so would not be a state function.

and want to get to the top of the mountain, there are many ways to go about it. You can go straight up the mountain, or you can spiral about the mountain, as two possibilities. The advantage to going straight up is that the path is shorter, but it is also steeper. A path spiraling around the mountain is less steep, but much longer. The amount of walking you end up doing is dependent on the path you take. Such quantities are considered *path-dependent.*

However, whichever path you take, you ultimately end up at the top of the mountain. Your altitude above the starting point is the same at the end of the climb regardless of which path you take. Your final altitude is said to be *path-independent.*

The change in altitude for your mountain climb can be considered a state function: it is path-independent. The amount of walking up the mountain is not a state function, because it is path-dependent.

Consider a physical or chemical process that a system undergoes. The process has initial conditions and final conditions, but there are any number of ways it can go from initial to final. A *state function* is any thermodynamic property whose value for the process is independent of the path. It depends only on the state of the system (in terms of state variables like p, V, T, n), not on its history or how the system got to that state. A thermodynamic property whose value for the process does depend on the path is not a state function. State functions are symbolized by capital letters; non-state functions are symbolized by lowercase letters. Internal energy is a state function. Work and heat are not.

State functions are different in another way. For an infinitesimal change in a system, the infinitesimal changes in the work, heat, and internal energy are represented as dw, dq, and dU. For a complete process, these infinitesimals are integrated from initial to final conditions. However, there is a slight difference in notation. When dw and dq are integrated, the result is the absolute amount of work w and heat q for the process. But when dU is integrated, the result is not the absolute U but the *change* in U, ΔU, for the process. Mathematically, this is written as

$$\int dw = w$$

$$\int dq = q \qquad \textbf{(2.13)}$$

but

$$\int dU = \Delta U$$

The same relationship exists for most of the other state functions as well. (There is one exception, which we will see in the next chapter.) The differentials dw and dq are called *inexact differentials,* meaning that their integrated values w and q are path-dependent. By contrast, dU is an *exact differential,* meaning that its integrated value ΔU is path-independent. All changes in state functions are exact differentials.

Another way to illustrate equations 2.13 is to note that

$$\Delta U = U_\mathrm{f} - U_\mathrm{i}$$

$$\text{but:} \quad w \neq w_\mathrm{f} - w_\mathrm{i} \quad \text{and} \quad q \neq q_\mathrm{f} - q_\mathrm{i}$$

The equations 2.13 imply that, for an infinitesimal change in a system,

$$dU = dq + dw$$

which is the infinitesimal form of the first law. But when we integrate this equation, we get

$$\Delta U = q + w$$

The difference in the treatment of q and w versus U is because U is a state function. We can know q and w absolutely, but they are dependent on the path that the system takes from initial to final conditions. ΔU does not, although we cannot know the absolute value of U for the initial and final states of a system.

Although these definitions might not seem useful, consider that any random change of any gaseous system might not be simply described as isothermal, adiabatic, and so on. However, in many cases, we can go from initial conditions to final conditions in small, ideal steps, and the overall change in a state function will be the combination of all of the steps. Since the change in a state function is path-independent, the change in the state function calculated in steps is the same as the change in the state function for a one-step process. We will see examples of this idea shortly.

If no work[†] is performed during the course of a process, then $dU = dq$ and $\Delta U = q$. There are two common conditions where work equals zero. The first is for a free expansion. The second is when the system does not change volume for a process. Since $dV = 0$, any expression that gives the work of the process will also be exactly zero. The relationship with heat under these conditions is sometimes written as

$$dU = dq_V \qquad \textbf{(2.14)}$$

$$\Delta U = q_V \qquad \textbf{(2.15)}$$

where the subscript V on q implies that the volume of the system during the change remains constant. Equation 2.15 is important because we can measure q values directly for many processes. If these processes occur at constant volume, we therefore know ΔU.

[†] Although we focus initially on pressure-volume work, there are other types of work, like electrical or gravitational work. Here we are assuming that none of these other types of work are performed on or by the system.

Example 2.7

A 1.00-L sample of gas at 1.00 atm pressure and 298 K expands isothermally and reversibly to 10.0 L. It is then heated to 500 K, compressed to 1.00 L, and then cooled to 25°C. What is ΔU for the overall process?

Solution

$\Delta U = 0$ for the overall process. Remember that a state function is a variable whose value depends on the instantaneous conditions of the system. Since the initial and final conditions of the system are the same, the system has the same absolute value of internal energy (whatever it might be), so that the overall change in the internal energy is zero.

2.5 Enthalpy

Although the internal energy represents the total energy of a system, and the first law of thermodynamics is based on the concept of internal energy, it is not always the best variable to work with. Equation 2.15 shows that the change in the internal energy is exactly equal to q—if the volume of the system remains constant for a particular process. However, the experimental condition of constant volume can be difficult to guarantee for many processes. Constant pressure, considering that many experiments occur exposed to the atmosphere, is often an easier experimental parameter.

Enthalpy is given the symbol H. The fundamental definition of enthalpy is

$$H \equiv U + pV \tag{2.16}$$

The pressure in equation 2.16 is the pressure of the system, p_{int}. Enthalpy is also a state function. Like internal energy, the absolute value of the enthalpy is unknowable, but we can determine *changes* in the enthalpy, dH:

$$dH = dU + d(pV) \tag{2.17}$$

The integrated form of this equation is

$$\Delta H = \Delta U + \Delta(pV) \tag{2.18}$$

Using the chain rule of calculus, we can rewrite equation 2.17 as

$$dH = dU + p\,dV + V\,dp$$

For a constant pressure process (which is more common in laboratory experiments), the $V\,dp$ term is zero because dp is zero. Using the original definition of dU, the equation becomes

$$dH = dq + dw + p\,dV$$

$$dH = dq - p\,dV + p\,dV$$

$$dH = dq \tag{2.19}$$

In terms of overall changes to a system, equation 2.19 can be integrated to get

$$\Delta H = q$$

Since the process occurs at constant pressure, the last equation is written like equation 2.15 as

$$\Delta H = q_p \tag{2.20}$$

Because the energy changes of so many processes are measured under conditions of constant pressure, *the change in enthalpy for a process is usually easier to measure than the change in internal energy.* As such, although the internal energy is the more fundamental quantity, the enthalpy is the more common.

Example 2.8

Indicate which state function is equal to heat for each process described.

a. The ignition of a sample in a bomb calorimeter, an unyielding, heavy metal chamber in which samples are burned for heat content analysis

b. The melting of an ice cube in a cup

c. The cooling down of the inside of a refrigerator

d. A fire in a fireplace

Solution

a. From the description, one can guess that a bomb calorimeter is a constant-volume system; therefore, the heat generated by the ignition of a sample equals ΔU.

b. If the cup is exposed to the atmosphere, it is subject to the (usually) constant pressure of the air and so the heat of the process is equal to ΔH.

c. A refrigerator does not change volume as it cools food, so the loss of heat from the inside equals ΔU.

d. A fire in a fireplace is usually exposed to the atmosphere, so the heat generated is also a measure of ΔH.

Example 2.9

A piston filled with 0.0400 mole of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. Calculate q, w, ΔU, and ΔH for the process.

Solution

Since 208 J of heat is going into the system, the total amount of energy is going up by 208 J, so $q = +208$ J. In order to calculate work, we can use equation 2.7:

$$w = -(0.0400\ \text{mol})\left(8.314\ \frac{\text{J}}{\text{mol·K}}\right)(310\ \text{K})\ \ln\left(\frac{375\ \text{mL}}{50.0\ \text{mL}}\right)$$

$$w = -208\ \text{J}$$

Since ΔU equals $q + w$,

$$\Delta U = +208\ \text{J} - 208\ \text{J}$$

$$\Delta U = 0\ \text{J}$$

We can use equation 2.18 to calculate ΔH, but we need to find the initial and final pressures so we can determine $\Delta(pV)$. Using the ideal gas law:

$$p_\text{i} = \frac{(0.0400\ \text{mol})(0.08205\ \frac{\text{L·atm}}{\text{mol·K}})(310\ \text{K})}{0.050\ \text{L}}$$

$$p_\text{i} = 20.3\ \text{atm}$$

and similarly:

$$p_\mathrm{f} = \frac{(0.0400\ \mathrm{mol})(0.08205\ \frac{\mathrm{L{\cdot}atm}}{\mathrm{mol{\cdot}K}})(310\ \mathrm{K})}{0.375\ \mathrm{L}} = 2.71\ \mathrm{atm}$$

To calculate $\Delta(pV)$, multiply the final pressure and volume together, then subtract the product of the initial pressure and volume:

$$\Delta(pV) = (2.71\ \mathrm{atm})(0.375\ \mathrm{L}) - (20.3\ \mathrm{atm})(0.0500\ \mathrm{L}) = 0$$

as expected for what is basically a Boyle's-law expansion of an ideal gas. Therefore $\Delta H = \Delta U$ and so

$$\Delta H = 0\ \mathrm{J}$$

Although the changes in the two state functions are equal (and zero) in this example, this is not always the case.

Because ΔH is a common state function, we base the definitions of some terms on enthalpy, not internal energy. The term *exothermic* is applied to any process where ΔH for the process is negative. In such cases, energy is being given off by the system into the surroundings. The term *endothermic* refers to any process where ΔH is positive. In these cases, energy is being absorbed by the system from the surroundings.

2.6 Changes in State Functions

Although we stated that we can know only the *change* in internal energy or enthalpy, so far we have mostly dealt with the overall change of a complete process. We have not considered infinitesimal changes in H or U in much detail.

Both the internal energy and the enthalpy of a given system are determined by the state variables of the system. For a gas, this means the amount, the pressure, the volume, and the temperature of the gas. We will initially assume an unchanging amount of gas (although this will change when we get to chemical reactions). So, U and H are determined by p, V, and T alone. But p, V, and T are related by the ideal gas law (for an ideal gas), so knowing any two you can determine the third. There are therefore only two independent state variables for a given amount of gas in a system. If we want to understand the infinitesimal change in a state function, we need only understand how it varies with respect to two of the three state variables of p, V, and T. The third one can be calculated from the other two.

Which two do we pick for internal energy and enthalpy? Although we can pick any two, in the mathematics that follow there will be advantages to picking a certain pair for each state function. For internal energy, we will use temperature and volume. For enthalpy, we will use temperature and pressure.

The total differential of a state function is written as the sum of the derivative of the function with respect to each of its variables. For example, dU is equal to the change in U with respect to temperature at constant volume plus the change in U with respect to volume at constant temperature. For the change in U written as $U(T, V) \rightarrow U(T + dT, V + dV)$, the infinitesimal change in internal energy is

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{2.21}$$

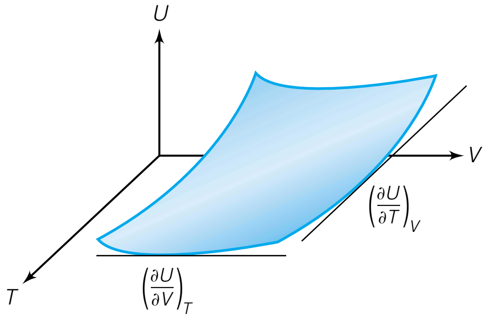

Figure 2.8 An illustration that the overall change in U can be separated into a change with respect to temperature [labeled $(\partial U/\partial T)_V$] and a change with respect to volume [labeled $(\partial U/\partial V)_T$].

Thus dU has one term that varies with temperature and one term that varies with volume. The two partial derivatives represent slopes in the plot of U versus T and V, and the total infinitesimal change in U, dU, can be written in terms of those slopes. Figure 2.8 illustrates a plot of U and the slopes that are represented by the partial derivatives.

Recall that there is another definition for dU: $dU = dq + dw = dq - p\,dV$. If we equate these two definitions of dU:

$$\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = dq - p\,dV$$

Solving for the change in heat, dq:

$$dq = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + p\,dV$$

Grouping the two terms in dV gives

$$dq = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV$$

If our gaseous system undergoes a change in which the volume does not change, then $dV = 0$ and the above equation simplifies to

$$dq = \left(\frac{\partial U}{\partial T}\right)_V dT \tag{2.22}$$

We can also rewrite this by dividing both sides of the equation by dT:

$$\frac{dq}{dT} = \left(\frac{\partial U}{\partial T}\right)_V$$

The change in heat with respect to temperature, which equals the change in the internal energy with respect to temperature at constant volume, is defined as the *constant volume heat capacity* of the system. (Compare this definition to that of equation 2.9, where we define the heat in terms of the change in temperature using a constant we called specific heat.) In terms of the partial derivative above,

$$\left(\frac{\partial U}{\partial T}\right)_V \equiv C_V \tag{2.23}$$

where we now use the symbol C_V for the constant volume heat capacity. Equation 2.22 can therefore be written as

$$dq = C_V\,dT \tag{2.24}$$

To evaluate the total heat, we integrate both sides of this infinitesimal equation to get

$$q_V = \int_{T_i}^{T_f} C_V \, dT = \Delta U \tag{2.25}$$

where the final equality is taken from the fact that $\Delta U = q$ for a constant-volume change. Equation 2.25 is the most general form for a constant-volume change. However, if the heat capacity is constant over the temperature range (for small temperature ranges not involving changes in phase, it is), it can be taken out of the integral to yield

$$\Delta U = C_V \int_{T_i}^{T_f} dT = C_V(T_f - T_i) = C_V \, \Delta T \tag{2.26}$$

For n moles of gas, this is rewritten simply as

$$\Delta U = n\overline{C}_V \, \Delta T \tag{2.27}$$

where $\overline{C}_V$ is the *molar heat capacity.* If the heat capacity does vary substantially with temperature, some expression for C_V in terms of temperature will have to be substituted in equation 2.25 and the integral evaluated explicitly. If this is the case, the temperatures for the integral limits must be expressed in kelvins.

If the heat capacity is divided by the mass of the system, it will have units of J/g·K or J/kg·K and is referred to as the *specific heat capacity* or, commonly, the *specific heat.* Care should be taken to note the units of a given heat capacity to determine if it is really a specific heat.

Example 2.10

Evaluate ΔU for 1.00 mole of oxygen, O_2, going from $-20.0°\text{C}$ to $37.0°\text{C}$ at constant volume, in the following cases. (ΔU will have units of J.)

a. It is an ideal gas with $\overline{C}_V = 20.78$ J/mol·K.

b. It is a real gas with an experimentally determined $\overline{C}_V = 21.6 + 4.18 \times 10^{-3}T - (1.67 \times 10^5)/T^2$.

Solution

a. Because we are assuming that the heat capacity is constant, we can use equation 2.27, where the change in temperature is 57°:

$$\Delta U = n\overline{C}_V \, \Delta T = (1.00 \text{ mol})\left(20.78 \frac{\text{J}}{\text{mol·K}}\right)(57.0°) = 1184 \text{ J}$$

Here, we are using the unit for $\overline{C}_V$ that includes the mole unit in the denominator.

b. Since the heat capacity varies with temperature, we have to integrate the expression in equation 2.25. We must also convert our temperatures to kelvins:

$$\Delta U = \int_{T_i}^{T_f} C_V \, dT = \int_{253 \text{ K}}^{310 \text{ K}} \left(21.6 + 4.18 \times 10^{-3}T - \frac{167{,}000}{T^2}\right) dT$$

Integrating term by term:

$$\Delta U = 21.6\ T + \frac{1}{2} \cdot 4.18 \times 10^{-3}T^2 + \frac{167{,}000}{T}\Bigg|_{253}^{310}$$

and evaluating at the limits:

$$\Delta U = 6696.0 + 200.0 + 538.7 - 5464.8 - 133.8 - 660.1 = 1176.8 \text{ J}$$

Notice the slight difference in the answers. Such slight differences may be lost in the significant figures of a calculation (as they would in this case), but in very precise measurements these differences will be noticed.

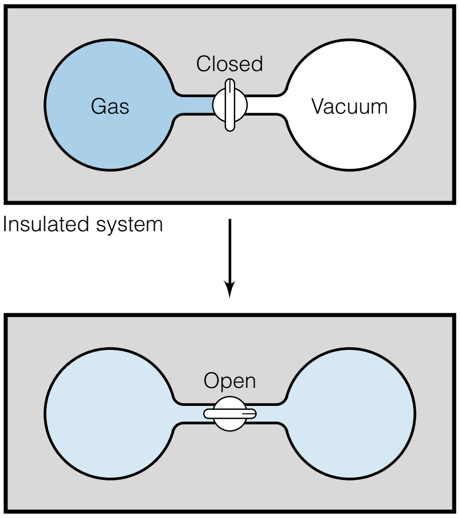

Figure 2.9 An adiabatic, free expansion of an ideal gas leads to some interesting conclusions about ΔU. See text for discussion.

There is one further conclusion about internal energy changes. Consider the change in ΔU for the process illustrated in Figure 2.9: an insulated system in which an ideal gas is in one chamber, and then a valve is opened and the gas expands into a vacuum. Because this is a free expansion, work is zero. The insulation keeps any heat from being exchanged between the system and the surroundings, so $q = 0$ also. This means that $\Delta U = 0$ for this process. By equation 2.21, this means that

$$0 = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dT$$

Barring the possible coincidence that the two terms might cancel each other out exactly, the right side of the equation will be zero only if both of the terms themselves are zero. The derivative in the first term, $(\partial U/\partial T)_V$, is *not* zero because temperature is a measure of energy of the system. As the temperature changes, of course the energy changes; this is what a nonzero heat capacity implies. Therefore dT, the change in temperature, must equal zero and the process is isothermic. Consider the second term, however. We know that dV is nonzero because the ideal gas expands, and in doing so changes its volume. In order for the second term to be zero, then, the partial derivative $(\partial U/\partial V)_T$ *must* be zero:

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad \text{for an ideal gas} \tag{2.28}$$

This derivative says that the change in internal energy with respect to volume changes *at constant temperature* must be zero for an ideal gas. Because we assume that in an ideal gas the individual particles do not interact with each other, a change in the volume of the ideal gas (which would tend to separate the individual particles more, on average) does not change the total energy if the temperature remains constant. In fact, equation 2.28 is one of the two criteria for an ideal gas. An ideal gas is any gas that (a) follows the ideal gas law as an equation of state, as discussed in Chapter 1, and (b) has an internal energy that does not change if the temperature of the gas does not change. For real gases, equation 2.28 does not apply and the total energy *will* change with volume. This is because there are interactions between the atoms and molecules of real gases.

One can do similar things with the infinitesimal for enthalpy, dH. We have already mentioned that we will use temperature and pressure for enthalpy. Hence,

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \tag{2.29}$$

If a change occurs at constant pressure, then $dp = 0$ and we have

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT$$

where we can now define a *constant-pressure heat capacity* C_p just as we defined C_V. Only now, we define our heat capacity in terms of H:

$$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p \tag{2.30}$$

Equation 2.30 means we can substitute C_p in the previous equation, so we get

$$dH = C_p\, dT$$

and integrate to get the total change in enthalpy for the temperature change:

$$\Delta H = \int_{T_i}^{T_f} C_p\, dT = q_p \tag{2.31}$$

where again we use the fact that ΔH equals q for a change that occurs under constant pressure. Equation 2.31 must be used if the heat capacity varies with temperature (see Example 2.10). If C_p is constant over the temperature range, then equation 2.31 can be simplified to

$$\Delta H = C_p\, \Delta T = q_p \tag{2.32}$$

The comments regarding units on C_V also apply to C_p (that is, you should keep track of whether a specific amount, in units of grams or moles, is specified or if it is actually part of the calculation). We can also define a molar heat capacity $\overline{C}_p$ for a process that occurs under constant pressure conditions.

Do not confuse the heat capacity at constant volume for heat capacity at constant pressure. For a gaseous system, they can be very different. For solids and liquids, they are not so different, but for solids and liquids the heat capacity can also vary with temperature. For a change in a gaseous system, you must know whether the change is a constant pressure change (called an *isobaric* change) or a constant volume change (called an *isochoric* change) in order to determine which heat capacity is the correct one for the calculation of heat, ΔU, ΔH, or both.

Finally, it can also be shown that for an ideal gas,

$$\left(\frac{\partial H}{\partial p}\right)_T = 0 \tag{2.33}$$

That is, the change in the enthalpy at constant temperature is also exactly zero. This is analogous to the situation for U.

2.7 Joule-Thomson Coefficients

Although we have been working with a lot of equations, all of them are ultimately based on two ideas: equations of state and the first law of thermodynamics. These ideas are ultimately based on the definition of total energy and various manipulations of that definition. In addition, we have seen several cases in which the equations of thermodynamics are simplified by the specification of certain conditions: adiabatic, free expansion, isobaric, and isochoric conditions are all restrictions on a process that simplify the mathematics of thermodynamics. Are there other useful restrictions?

Another useful restriction based on the first law of thermodynamics is described by the Joule-Thomson experiment, illustrated in Figure 2.10. An adiabatic system is set up and filled with a gas on one side of a porous barrier. This gas has some temperature T_1, a fixed pressure p_1, and an initial volume V_1. A piston pushes on the gas and forces all of it through the porous barrier, so the final volume on this side of the barrier is zero. On the other side of the barrier, a second piston moves out as the gas diffuses to the other side, where it will have a temperature T_2, a fixed pressure p_2, and a volume V_2. Initially, the volume on the right side of the barrier is zero. Since the gas is being forced through a barrier, it is understood that $p_1 > p_2$. Even though the pressures on

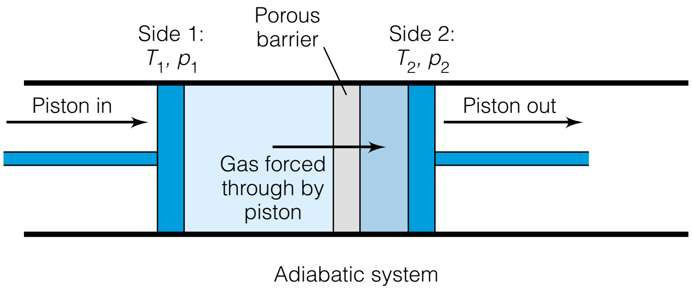

Figure 2.10 The isenthalpic experiment of Joule and Thomson. A description is given in the text.

either side are fixed, it should be understood that the gas experiences a drop in pressure as it is forced from one side to the other.

On the left side, work is done on the gas, which contributes positively to the overall change in energy. On the right side, the gas does work, contributing negatively to the overall change in energy. The net work w_{net} performed by the system after the first piston is completely pushed in is

$$w_{\text{net}} = p_1 V_1 - p_2 V_2$$

Since the system is adiabatic, $q = 0$, so $\Delta U_{\text{net}} = w_{\text{net}}$, but we will write ΔU as the internal energy of the gas on side 2 minus the internal energy of the gas on side 1:

$$w_{\text{net}} = U_2 - U_1$$

Equating the two expressions for w_{net}:

$$p_1 V_1 - p_2 V_2 = U_2 - U_1$$

and rearranging:

$$U_1 + p_1 V_1 = U_2 + p_2 V_2$$

The combination $U + pV$ is the original definition of H, the enthalpy, so for the gas in this Joule-Thomson experiment,

$$H_1 = H_2$$

or, for the gas undergoing this process, the *change* in H is zero:

$$\Delta H = 0$$

Since the enthalpy of the gas does not change, the process is called *isenthalpic*. What are some consequences of this isenthalpic process?

Although the change in enthalpy is zero, the change in temperature is not. What is the change in temperature accompanying the pressure drop for this isenthalpic process? That is, what is $(\partial T/\partial p)_H$? We can actually measure this derivative experimentally, using an apparatus like the one in Figure 2.10.

The *Joule-Thomson coefficient* μ_{JT} is defined as the change in temperature of a gas with pressure at constant enthalpy:

$$\mu_{\text{JT}} = \left(\frac{\partial T}{\partial p}\right)_H \tag{2.34}$$

A useful approximation of this definition is

$$\mu_{\text{JT}} \approx \left(\frac{\Delta T}{\Delta p}\right)_H$$

For an ideal gas, μ_{JT} is exactly zero, since enthalpy depends only on temperature (that is, at constant enthalpy, temperature is also constant). However, for real gases, the Joule-Thomson coefficient is not zero, and the gas will change temperature for the isenthalpic process. Remembering from the cyclic rule of partial derivatives that

$$\left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial p}{\partial H}\right)_T = -1$$

we can rewrite this as

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p}$$

and, recognizing that the left side is μ_{JT} and the denominator of the fraction is simply the heat capacity at constant pressure, we have

$$\mu_{JT} = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{C_p} \tag{2.35}$$

This equation verifies that μ_{JT} is zero for an ideal gas, since $(\partial H/\partial p)_T$ is zero for an ideal gas. Not for *real* gases, however. Further, if we measure μ_{JT} for real gases and also know their heat capacities, we can use equation 2.35 to calculate $(\partial H/\partial p)_T$ for a real gas, which is a quantity (the change in enthalpy as pressure changes but at constant temperature) that is difficult or impossible to measure by direct experiment.

Example 2.11

If the Joule-Thomson coefficient for carbon dioxide, CO_2, is 0.6375 K/atm, estimate the final temperature of carbon dioxide at 20 atm and 100°C that is forced through a barrier to a final pressure of 1 atm.

Solution

Using the approximate form of the Joule-Thomson coefficient:

$$\mu_{JT} \approx \left(\frac{\Delta T}{\Delta p}\right)_H$$

Δp in this process is -19 atm (the negative sign meaning that the pressure is going *down* by 19 atm). Therefore, we have

$$\left(\frac{\Delta T}{-19 \text{ atm}}\right)_H = 0.6375 \text{ K/atm}$$

Multiplying through:

$$\Delta T = -12 \text{ K}$$

which means that the temperature drops from 100°C to about 88°C.

The Joule-Thomson coefficient of real gases varies with temperature and pressure. Table 2.2 lists some experimentally determined μ_{JT} values. Under some conditions, the Joule-Thomson coefficient is negative, meaning that as

Table 2.2 Joule-Thomson coefficients of various gases (K/atm)

p (atm)	T = −150°C	−100°C	−50°C	0°C	50°C	100°C	150°C	200°C
Air, no water or carbon dioxide								
1	—	0.5895	0.3910	0.2745	0.1956	0.1355	0.0961	0.0645
20	—	0.5700	0.3690	0.2580	0.1830	0.1258	0.0883	0.0580
60	0.0450	0.4820	0.3195	0.2200	0.1571	0.1062	0.0732	0.0453
100	0.0185	0.2775	0.2505	0.1820	0.1310	0.0884	0.0600	0.0343
140	−0.0070	0.1360	0.1825	0.1450	0.1070	0.0726	0.0482	0.0250
180	−0.0255	0.0655	0.1270	0.1100	0.0829	0.0580	0.0376	0.0174
200	−0.0330	0.0440	0.1065	0.1090	0.0950	—	—	—
Argon								
1	1.812	0.8605	0.5960	0.4307	0.3220	0.2413	0.1845	0.1377
20	—	0.8485	0.5720	0.4080	0.3015	0.2277	0.1720	0.1280
60	−0.0025	0.6900	0.4963	0.3600	0.2650	0.1975	0.1485	0.1102
100	−0.0277	0.2820	0.3970	0.3010	0.2297	0.1715	0.1285	0.0950
140	−0.0403	0.1137	0.2840	0.2505	0.1947	0.1490	0.1123	0.0823
180	−0.0595	0.0560	0.2037	0.2050	0.1700	0.1320	0.0998	0.0715
200	−0.0640	0.0395	0.1860	0.1883	0.1580	0.1255	0.0945	0.0675
Carbon dioxide								
1	—	—	2.4130	1.2900	0.8950	0.6490	0.4890	0.3770
20	—	—	−0.0140	1.4020	0.8950	0.6375	0.4695	0.3575
60	—	—	−0.0150	0.0370	0.8800	0.6080	0.4430	0.3400
100	—	—	−0.0160	0.0215	0.5570	0.5405	0.4155	0.3150
140	—	—	−0.0183	0.0115	0.1720	0.4320	0.3760	0.2890
180	—	—	−0.0228	0.0085	0.1025	0.3000	0.3102	0.2600
200	—	—	−0.248	0.0045	0.0930	0.2555	0.2910	0.2455
Nitrogen								
1	1.2659	0.6490	0.3968	0.2656	0.1855	0.1292	0.0868	0.0558
20	1.1246	0.5958	0.3734	0.2494	0.1709	0.1173	0.0776	0.0472
60	0.0601	0.4506	0.3059	0.2088	0.1449	0.0975	0.0628	0.0372
100	0.0202	0.2754	0.2332	0.1679	0.1164	0.0768	0.0482	0.0262
140	−0.0056	0.1373	0.1676	0.1316	0.0915	0.0582	0.0348	0.0168
180	−0.0211	0.0765	0.1120	0.1015	0.0732	0.0462	0.0248	0.0094
200	−0.0284	0.0587	0.0906	0.0891	0.0666	0.0419	0.0228	0.0070

Helium[a]

p (atm)	160 K	200 K	240 K	280 K	320 K	360 K	400 K	440 K
<200	−0.0574	−0.0594	−0.0608	−0.0619	−0.0629	−0.0637	−0.0643	−0.0645

Source: R. H. Perry and D. W. Green, *Perry's Chemical Engineers' Handbook*, 6th ed., McGraw-Hill, New York, 1984.

[a] Below 200 atm, there is little variation in the value of μ_{JT} for helium. (Also note that the helium data use Kelvin temperatures.)

the pressure drops the temperature goes *up*: it gets hotter upon expansion! At some lower temperature, the Joule-Thomson coefficient becomes positive, and then as pressure drops, the temperature of the gas drops as well. The temperature at which the Joule-Thomson coefficient goes from negative to positive is called the *inversion temperature.* In order to cool gases down using the Joule-Thomson method, a gas must be below its inversion temperature.

The Joule-Thomson effect is used to liquefy gases, since one can engineer a system where a gas is repeatedly compressed and expanded, decreasing its temperature, until the temperature drops so low that it condenses into a liquid. Liquid nitrogen and oxygen are commonly prepared that way, on a vast industrial scale. However, a gas must be below its inversion temperature in order for the Joule-Thomson effect to work in the proper direction of decreasing temperature! Gases that have very low inversion temperatures must be cooled before using a sort of Joule-Thomson expansion to liquefy them. Before this was widely realized, it was thought that some gases were "permanent gases," because they could not be liquefied by "ordinary" means. (Such gases were first described by Michael Faraday in 1845, because he was unable to liquefy them.) They included hydrogen, oxygen, nitrogen, nitric oxide, methane, and the first four noble gases. Nitrogen and oxygen were easily liquefied by performing a cyclic Joule-Thomson expansion on them, and the other gases soon followed. However, the inversion temperatures of hydrogen and helium are so low (about 202 K and 40 K, respectively) that they have to be precooled substantially before any kind of Joule-Thomson expansion will cool them further. Hydrogen was finally liquefied by the Scottish physicist James Dewar in 1898, and helium in 1908 by the Dutch physicist Heike Kamerlingh-Onnes (who used liquid helium to discover superconductivity).

2.8 More on Heat Capacities

Recall that we defined two different heat capacities, one for a change in a system kept at constant volume, and one for a change in a system kept at constant pressure. We labeled them C_V and C_p. What is the relationship between the two?

We start with an equation that eventually yielded equation 2.22. The relevant equation is

$$dq = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV \tag{2.36}$$

where p is the external pressure. We have defined the derivative $(\partial U/\partial T)_V$ as C_V, so we can rewrite the equation as

$$dq = C_V\, dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV$$

So far, we have imposed no conditions on the system in deriving the above expression, other than the sample being an ideal gas. We now impose the additional condition that the pressure be kept constant. Nothing really changes, since the infinitesimal change in heat dq is expressed in terms of a change in temperature, dT, and a change in volume, dV. We can therefore write the above equation as

$$dq_p = C_V\, dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV$$

where dq now has the subscript p. If we divide both sides of the equation by dT, we get

$$\left(\frac{\partial q}{\partial T}\right)_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

Note that the derivative $\partial V/\partial T$ has a p subscript, due to our specifying that this is for constant-pressure conditions. Also note that the expression is a *partial* derivative, because the quantities in the numerators depend on multiple variables. (Other derivatives have also been expressed as partial derivatives.) Since $dH = dq_p$, we can substitute on the left side of the equation to get

$$\left(\frac{\partial H}{\partial T}\right)_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

The term $(\partial H/\partial T)_p$ has already been defined as the heat capacity at constant pressure, C_p. We now have a relationship between C_V and C_p:

$$C_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p \tag{2.37}$$

If the system is composed of an ideal gas, this is straightforward to evaluate. The change in internal energy at constant temperature is exactly zero (that's one of the defining features of an ideal gas). We can also use the ideal gas law to determine the derivative $(\partial V/\partial T)_p$:

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p}$$

Substituting into equation 2.37:

$$C_p = C_V + (0 + p)\,\frac{nR}{p}$$

$$C_p = C_V + nR$$

or, for molar quantities:

$$\overline{C_p} = \overline{C_V} + R \tag{2.38}$$

for an ideal gas. This is an extremely simple and useful result.

The kinetic theory of gases (to be considered in a future chapter) leads to the result that, for a monatomic ideal gas,

$$\overline{C_V} = \frac{3}{2}R = 12.471\,\frac{\text{J}}{\text{mol·K}} \tag{2.39}$$

Therefore, by equation 2.38,

$$\overline{C_p} = \frac{5}{2}R = 20.785\,\frac{\text{J}}{\text{mol·K}} \tag{2.40}$$

Gases like Ar and Ne and He have constant-pressure heat capacities around 20.8 J/mol·K, which is not surprising. The lighter inert gases are good approximations of ideal gases.*

Ideal gases have a temperature-invariant heat capacity; real gases do not. Most attempts to express the heat capacity of real gases use a power series, in either of the two following forms:

$$C_p = a + bT + cT^2$$

$$C_p = a + bT + \frac{c}{T^2}$$

where a, b, and c are experimentally determined constants. Example 2.10, along with equation 2.31, illustrates the proper way to determine changes in state functions using heat capacities of this form.

---

*Kinetic theory of gases also predicts that for ideal diatomic or linear molecules, $\overline{C_V} = \frac{5}{2}R$; for ideal nonlinear molecules, $\overline{C_V} = \frac{7}{2}R$. $\overline{C_p}$ is thus $\frac{7}{2}R$ and $\frac{9}{2}R$, respectively. (We include this to illustrate that thermodynamics isn't just applicable to monatomic gases!)

Recall that, for an adiabatic process,

$$dU = dw$$

because heat is exactly zero. From equation 2.21, we also know that

$$dU = C_V\, dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V\, dT \quad \text{for an ideal gas}$$

where the final equality recognizes that the partial derivative $(\partial U/\partial V)_T$ equals zero for an ideal gas. Therefore, for an infinitesimal adiabatic process,

$$dw = C_V\, dT$$

Integrating for the overall adiabatic process,

$$w = \int_{T_\mathrm{i}}^{T_\mathrm{f}} C_V\, dT \tag{2.41}$$

For a constant heat capacity,

$$w = C_V\, \Delta T \tag{2.42}$$

For anything other than 1 mole, we must use the molar heat capacity, $\overline{C_V}$:

$$w = n\overline{C_V}\, \Delta T \tag{2.43}$$

If the heat capacity is not constant over the temperature range, equation 2.41 must be used with the proper expression for C_V to calculate the work of the change.

Example 2.12

Consider 1 mole of an ideal gas at an initial pressure of 1.00 atm and initial temperature of 273.15 K. Assume it expands adiabatically against a pressure of 0.435 atm until its volume doubles. Calculate the work, the final temperature, and the ΔU of the process.

Solution

The volume change of the process must be determined first. From the initial conditions, we can calculate the initial volume, and then its change:

$$(1.00\ \text{atm})V_\mathrm{i} = (1\ \text{mol})\left(0.08205\ \frac{\text{L·atm}}{\text{mol·K}}\right)(273.15\ \text{K})$$

$$V_\mathrm{i} = 22.4\ \text{L}$$

If the volume is doubled during the process, then the final volume is 44.8 L, and the change in volume is 44.8 L − 22.4 L = 22.4 L.

The work performed is calculated simply by

$$w = -p_\text{ext}\, \Delta V$$

$$w = -(0.435\ \text{atm})(22.4\ \text{L})\left(\frac{101.32\ \text{J}}{\text{L·atm}}\right) = -987\ \text{J}$$

Because $q = 0$, $\Delta U = w$, so that

$$\Delta U = -987\ \text{J}$$

The final temperature can be calculated using equation 2.43, recognizing that for an ideal gas the heat capacity at constant volume is $\frac{3}{2}R$, or 12.47 J/mol·K. Therefore,

$$-987\text{ J} = (1\text{ mol})\left(12.47\frac{\text{J}}{\text{mol·K}}\right)\Delta T$$

$$\Delta T = -79.1\text{ K}$$

With an initial temperature of 273.15 K, the final temperature is about 194 K.

For an adiabatic process, the infinitesimal amount of work done can now be determined from two expressions:

$$dw = -p_{\text{ext}}\,dV$$

$$dw = n\overline{C}_V\,dT$$

Equating the two:

$$-p_{\text{ext}}\,dV = n\overline{C}_V\,dT$$

If the adiabatic process is reversible, then $p_{\text{ext}} = p_{\text{int}}$ and we can use the ideal gas law to substitute for p_{int} in terms of the other state variables. We get

$$-\frac{nRT}{V}\,dV = n\overline{C}_V\,dT$$

Bringing the temperature variables to the right side, we find that

$$-\frac{R}{V}\,dV = \frac{\overline{C}_V}{T}\,dT$$

The variable n has canceled. We can integrate both sides of the equation and, assuming that $\overline{C}_V$ is constant over the change, we find (recognizing that $\int 1/x\,dx = \ln x$) that

$$-R\ln V\big|_{V_\text{i}}^{V_\text{f}} = \overline{C}_V\,\ln T\big|_{T_\text{i}}^{T_\text{f}}$$

Using the properties of logarithms and evaluating each integral at its limits, we get

$$-R\ln\frac{V_\text{f}}{V_\text{i}} = \overline{C}_V\,\ln\frac{T_\text{f}}{T_\text{i}} \tag{2.44}$$

for an adiabatic, reversible change in an ideal gas. Again using properties of logarithms, we can get rid of the negative sign by taking the reciprocal of the expression inside the logarithm:

$$R\ln\frac{V_\text{i}}{V_\text{f}} = \overline{C}_V\,\ln\frac{T_\text{f}}{T_\text{i}}$$

Recognizing that $\overline{C}_p = \overline{C}_V + R$, we rearrange it as $\overline{C}_p - \overline{C}_V = R$ and substitute:

$$(\overline{C}_p - \overline{C}_V)\ln\frac{V_\text{i}}{V_\text{f}} = \overline{C}_V\,\ln\frac{T_\text{f}}{T_\text{i}}$$

Dividing through by $\overline{C}_V$:

$$\frac{(\overline{C}_p - \overline{C}_V)}{\overline{C}_V}\ln\frac{V_\text{i}}{V_\text{f}} = \ln\frac{T_\text{f}}{T_\text{i}}$$

The expression $(\overline{C}_p - \overline{C}_V)/\overline{C}_V$ is usually defined as γ:

$$\gamma \equiv \frac{(\overline{C}_p - \overline{C}_V)}{\overline{C}_V} \tag{2.45}$$

We can rearrange the equation relating volumes and temperatures above to get

$$\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)^{\gamma} = \frac{T_\mathrm{f}}{T_\mathrm{i}} \tag{2.46}$$

It can be shown that γ equals $\frac{2}{3}$ for a monatomic ideal gas.[*] Thus,

$$\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)^{2/3} = \frac{T_\mathrm{f}}{T_\mathrm{i}} \tag{2.47}$$

for an adiabatic, reversible change of a monatomic ideal gas. If we did this in terms of pressure instead of volume, we would find that

$$\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right)^{2/5} = \frac{T_\mathrm{f}}{T_\mathrm{i}} \tag{2.48}$$

If equations 2.47 and 2.48 were combined algebraically, one would derive

$$p_1 V_1{}^{5/3} = p_2 V_2{}^{5/3} \tag{2.49}$$

which is a special case of Boyle's law for ideal gases undergoing reversible, adiabatic processes. However, in this case, it is not assumed that the temperature is held constant.

Example 2.13

For an adiabatic, reversible change in 1 mole of an inert monatomic gas, the pressure changes from 2.44 atm to 0.338 atm. If the initial temperature is 339 K, what is the final temperature?

Solution

Using equation 2.48,

$$\left(\frac{0.338\ \mathrm{atm}}{2.44\ \mathrm{atm}}\right)^{2/5} = \frac{T_\mathrm{f}}{339\ \mathrm{K}}$$

Solving:

$$T_\mathrm{f} = 154\ \mathrm{K}$$

2.9 Phase Changes

So far, we have considered only physical changes of gaseous systems. We have not yet considered changes in phase, nor chemical changes. We introduce the application of the ideas discussed so far to those kinds of processes now, starting with changes in phase.

In most cases, changes in phase (solid $\rightleftharpoons$ liquid, liquid $\rightleftharpoons$ gas, solid $\rightleftharpoons$ gas) occur under experimental conditions of constant pressure, so that the heat involved, q, is also equal to ΔH.[†] For example, for the melting of ice at its normal melting point of 0°C:

$$\mathrm{H_2O}\ (\mathrm{s}, 0^\circ\mathrm{C}) \longrightarrow \mathrm{H_2O}\ (\ell, 0^\circ\mathrm{C})$$

a certain amount of heat is required per gram or per mole in order to change the phase. However, during the phase change, the temperature does not change.

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[*] $\overline{C}_p$ and $\overline{C}_V$ have different values for ideal polyatomic gases, so γ also has a different value in those cases. We won't consider this topic further here.

[†] Changes in pressure can also cause phase changes. We will consider this in Chapter 6.

H_2O can exist at 0°C as either a solid or a liquid. Because there is no ΔT, equation 2.9 does not apply. Instead, the amount of heat involved is proportional to the amount of material. The proportionality constant is called the *heat of fusion,* $\Delta_{\text{fus}}H$, so that we have a simpler equation:

$$q = m \cdot \Delta_{\text{fus}}H \tag{2.50}$$

The word *fusion* is a synonym for "melting." If amount m is given in units of grams, $\Delta_{\text{fus}}H$ has units of J/g. If the amount is given in units of moles, equation 2.50 is more properly written as

$$q = n \cdot \overline{\Delta_{\text{fus}}H} \tag{2.51}$$

and $\overline{\Delta_{\text{fus}}H}$ is a molar quantity with units of J/mol. Since freezing and melting are simply opposite processes, equations 2.50 and 2.51 are valid for both processes. The process itself dictates whether the label exothermic or endothermic is appropriate. For melting, heat must be put into the system, so the process is endothermic and the value of ΔH for the process is positive. For freezing, heat must be removed from the system, so freezing is exothermic and the value for ΔH is negative.

Example 2.14

The heat of fusion $\Delta_{\text{fus}}H$ for water is 334 J/g.

a. How much heat is required to melt 59.5 g of ice (about one large ice cube)?

b. What is the value of ΔH for this process?

Solution

a. According to equation 2.50,

$$q = (59.5 \text{ g})(334 \text{ J/g})$$

$$q = 1.99 \times 10^4 \text{ J}$$

b. Because heat must be put into the system in order to go from solid to liquid, the ΔH for this process should reflect the fact that the process is endothermic. Therefore, $\Delta H = 1.99 \times 10^4$ J.

Changes in volume when going from solid to liquid, or from liquid to solid, are usually negligible, so that $\Delta H \approx \Delta U$. (Water is an obvious exception. It expands approximately 10% when freezing.) On the other hand, the change in volume in going from a liquid to a gas (or a solid to a gas) is considerable:

$$H_2O\ (\ell,\ 100^\circ C) \longrightarrow H_2O\ (g,\ 100^\circ C)$$

In going from a liquid to a gas, a process called *vaporization,* again the temperature stays constant while the phase change occurs, and the amount of heat necessary is again proportional to the amount. This time, the proportionality constant is called the *heat of vaporization,* $\Delta_{\text{vap}}H$, but the form of the equation for calculating the heat involved is similar to equation 2.50:

$$q = m \cdot \Delta_{\text{vap}}H \quad \text{for amounts in grams} \tag{2.52}$$

or equation 2.51:

$$q = n \cdot \overline{\Delta_{\text{vap}}H} \quad \text{for amounts in moles} \tag{2.53}$$

The heat involved in the reverse process, *condensation,* can also be calculated with equations 2.52 and 2.53 with the understanding that once again we will have to keep track of which direction heat is going. When determining work for a vaporization or sublimation, it is common to neglect the volume of the condensed phase, which is usually negligible. The following example illustrates.

Example 2.15

Calculate q, w, ΔH, and ΔU for the vaporization of 1 g of H_2O at 100°C and 1.00 atm pressure. The $\Delta_{\text{vap}}H$ of H_2O is 2260 J/g. Assume ideal gas behavior. The density of H_2O at 100°C is 0.9588 g/cm^3.

Solution

Using equation 2.52, the heat and ΔH for the process are straightforward:

$$q = (1\text{ g})(2260\text{ J/g}) = 2260\text{ J} \quad \text{into the system}$$

$$q = \Delta H = +2260\text{ J}$$

In order to calculate the work, we need the volume change for the vaporization. For the process $H_2O\ (\ell) \rightarrow H_2O\ (g)$, the change in volume is

$$\Delta V = V_{\text{gas}} - V_{\text{liq}}$$

Using the ideal gas law, we can calculate the volume of the water vapor at 100°C = 373 K:

$$V_{\text{gas}} = \frac{(0.0555\text{ mol})(0.08205\ \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(373\text{ K})}{1.00\text{ atm}}$$

$$V_{\text{gas}} = 1.70\text{ L}$$

The volume of liquid H_2O at 100°C is 1.043 cm^3, or 0.001043 L. Therefore,

$$\Delta V = V_{\text{gas}} - V_{\text{liq}} = 1.70\text{ L} - 0.001043\text{ L} \approx 1.70\text{ L} = V_{\text{gas}}$$

In this step, we show that the volume of the liquid is negligible with respect to the volume of the gas, so to a very good approximation $\Delta V = V_{\text{gas}}$. To calculate the work of the vaporization:

$$w = -p_{\text{ext}}\,\Delta V$$

$$w = -(1.00\text{ atm})(1.70\text{ L})\left(\frac{101.32\text{ J}}{1\text{ L}\cdot\text{atm}}\right)$$

$$w = -172\text{ J}$$

Since $\Delta U = q + w$,

$$\Delta U = 2260\text{ J} - 172\text{ J}$$

$$\Delta U = 2088\text{ J}$$

This is an example where the change in enthalpy does not equal the change in internal energy.

Table 2.3 $\Delta_{\text{fus}}H$ and $\Delta_{\text{vap}}H$ for various substances (J/g)

Material	$\Delta_{\text{fus}}H$	$\Delta_{\text{vap}}H$
Al	393.3	10,886
Al_2O_3	1,070	
CO_2	180.7	573.4 (sublimes)
F_2	26.8	83.2
Au	64.0	1,710
H_2O	333.5	2,260
Fe	264.4	6,291
NaCl	516.7	2,892
C_2H_5OH, ethanol	188.99	838.3
C_6H_6, benzene	127.40	393.8
C_6H_{14}, hexane	151.75	335.5

Table 2.3 lists some values for $\Delta_{\text{fus}}H$ and $\Delta_{\text{vap}}H$ for various substances. The values for $\Delta_{\text{fus}}H$ and $\Delta_{\text{vap}}H$ are indicative of how much energy is necessary to change the phase, and as such are related to the strength of the interatomic or intermolecular interactions in the materials. Water, for example,

has an unusually large heat of vaporization for such a small molecule. This is caused by the strong hydrogen bonding between water molecules. It takes a lot of energy to separate the individual water molecules (which is about what happens during the vaporization process), and the high heat of vaporization reflects that fact.

2.10 Chemical Changes

When a chemical reaction occurs, the chemical identities of the system are changing. Although most of the equations and definitions we have considered so far are still directly applicable, we need to expand the applicability of ΔU and ΔH.

It should be understood that all chemical substances have a total internal energy and enthalpy. When a chemical change occurs, the change in the internal energy or enthalpy that accompanies the chemical change is equal to the total enthalpy of the final conditions, the products, minus the total enthalpy of the initial conditions, the reactants. That is,

$$\Delta_{\text{rxn}}H = H_{\text{f}} - H_{\text{i}}$$

$$\Delta_{\text{rxn}}H = H_{\text{products}} - H_{\text{reactants}}$$

where we are using $\Delta_{\text{rxn}}H$ to indicate the change in enthalpy for the chemical reaction. $\Delta_{\text{rxn}}U$ is the equivalent for internal energy. Figure 2.11 illustrates this idea. In each graph, one line represents the total enthalpy of the products; the other is the total enthalpy of the reactants. The difference between the lines represents the change in enthalpy for the reaction, $\Delta_{\text{rxn}}H$. In one case, Figure 2.11a, the amount of enthalpy in the system is going down. That is, the system is giving off energy into the surroundings. This is an example of an exothermic process. In the other case, Figure 2.11b, the amount of enthalpy in the system is going up. This means that energy is going into the system, so this is an example of an endothermic process.

The change in energy of a chemical process depends on the conditions of the process, like temperature and pressure. The standard condition of pressure is 1 bar (which is almost equal to 1 atm, so use of 1 atm as the standard condition of pressure does not impart too much error). There is no defined standard temperature, although many thermodynamic measurements are reported

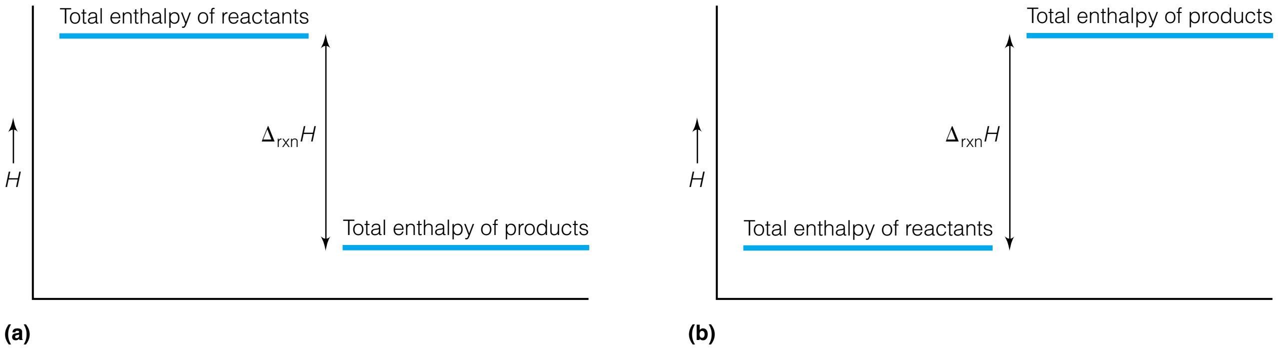

Figure 2.11 A graphical interpretation of the statement that $\Delta_{\text{rxn}}H$ for a chemical process is the difference between the total enthalpies of the products minus the total enthalpies of the reactants. (a) An exothermic reaction, since the total energy of the system is going down (meaning that energy is given off). (b) An endothermic reaction, since the total energy of the system is going up (meaning that the energy is entering the system).

for 25.0°C. To indicate that the energy change is meant to imply standard conditions, a ° superscript is attached to the symbol. We therefore speak of $\Delta_{\text{rxn}}H°$, $\Delta_{\text{rxn}}U°$, etc. Temperatures are usually specified as well.

Although we have defined $\Delta_{\text{rxn}}H$ for a chemical process, values of $\Delta_{\text{rxn}}H$ are not determined by evaluating the difference $H_f - H_i$. This is because absolute values for enthalpy cannot be determined. Only relative values, *changes* in enthalpy, can be measured. What we need is a set of chemical reactions whose $\Delta_{\text{rxn}}H$ values can serve as standards against which all other $\Delta_{\text{rxn}}H$ values can be measured.

The method for determining $\Delta_{\text{rxn}}H$ for chemical processes is based on the ideas of the chemist Germain Henri Hess (1802–1850), who was born in Switzerland but spent most of his life in Russia. Hess can be considered the founder of the subtopic of thermodynamics called *thermochemistry*. Hess studied the energy changes (in terms of heat, mostly) of chemical reactions. Ultimately, he realized that several key ideas are important in studying the energy changes that accompany chemical reactions. In a modern form (Hess lived before the field of thermodynamics was fully established), they are:

- Specific chemical changes are accompanied by a characteristic change in energy.
- New chemical changes can be devised by combining known chemical changes. This is done algebraically.
- The change in energy of the combined chemical reaction is the equivalent algebraic combination of the energy changes of the component chemical reaction.

The above ideas are collectively known as *Hess's law* and are the fundamental basis of thermodynamics as applied to chemical reactions. Because we are treating chemical equations algebraically, we need to keep the following two thoughts in mind as we combine their energy changes algebraically.

- When a reaction is reversed, the energy change of the reaction reverses sign. This is a consequence of enthalpy being a state function.
- When multiples of a reaction are considered, the same multiple of the energy change must be used. This applies to fractional as well as whole-number multiples. This is a consequence of enthalpy being an extensive property.

Hess's law means that we can take the measured changes in energy for reactions and combine them in whatever way we need, and the change in energy for the overall reaction is just some algebraic sum of the known energies. Measured energy changes for chemical reactions can be tabulated, and for the appropriate combination of chemical reactions, we need only consult the tables and perform the proper algebra. Hess's law is a direct consequence of enthalpy being a state function.

The question now is, what reactions should we tabulate? There is an inexhaustible supply of possible chemical reactions. Do we tabulate the energy changes of all of them? Or of only a selected few? And which few?

Enthalpy changes of only one kind of chemical reaction need to be tabulated (although it is not uncommon to see tables of enthalpy changes of other reactions, like combustion reactions). A *formation reaction* is any reaction making 1 mole of a product using, as reactants, the product's constituent elements in their standard states.* We use the symbol $\Delta_f H$ to stand for the enthalpy change

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*The standard state of an element is the pure substance at 1 bar (previously, 1 atm) and having the specified allotropic form, if necessary. Although there is no specified standard temperature, many references use 25.0°C as the designated temperature.

of a formation reaction, called the *enthalpy of formation* or (more loosely) the *heat of formation.* As an example,

$$\tfrac{1}{2}N_2\ (g) + O_2\ (g) \longrightarrow NO_2\ (g)$$

is the formation reaction for NO_2. As a counterexample,

$$2NO_2\ (g) + \tfrac{1}{2}O_2\ (g) \longrightarrow N_2O_5\ (g)$$

is *not* the formation reaction for N_2O_5 because the reactants are not all the elements that compose N_2O_5. For tabulation purposes, most of the $\Delta_f H$ values are measured with respect to the standard state of the reactants, so they are usually $\Delta_f H^\circ$ (with ° to indicate standard state).

Example 2.16

Determine whether the following reactions are formation reactions or not, and if not, why. Assume that the reactions are occurring under standard conditions.

a. $H_2\ (g) + \tfrac{1}{2}O_2\ (g) \rightarrow H_2O\ (\ell)$
b. $Ca\ (s) + 2\ Cl\ (g) \rightarrow CaCl_2\ (s)$
c. $2\ Fe\ (s) + 3S\ (\text{rhombic}) + 4O_3\ (g) \rightarrow Fe_2(SO_4)_3\ (s)$
d. $6C\ (s) + 6H_2\ (g) + 3O_2\ (g) \rightarrow C_6H_{12}O_6\ (s)$ (glucose)

Solution

a. Yes, this is the formation reaction for liquid water.
b. No. The "standard form" of chlorine is a diatomic molecule.
c. No. The "standard form" of elemental oxygen is the diatomic molecule. The O_3 in the formula is the allotrope ozone.
d. Yes, this is the formation reaction for glucose.

Notice that, by definition, the enthalpy of formation for elements in their standard state is exactly zero. This is because, no matter what the absolute enthalpies of the product and reactant are, they are the same, so the change in enthalpy for the reaction is zero. For example,

$$Br_2\ (\ell) \longrightarrow Br_2\ (\ell)$$

is the formation reaction for elemental bromine. Since there is no change in the chemical identity over the course of the reaction, the enthalpy change is zero and we say that $\Delta_f H^\circ = 0$ for elemental bromine. The same situation exists for all elements in their standard states.

The reason we focus on formation reactions is because it is the changes in enthalpy for formation reactions that are tabulated and used to determine enthalpy changes for chemical processes. This is because any chemical reaction can be written as an algebraic combination of formation reactions. Hess's law therefore dictates how the $\Delta_f H^\circ$ values are combined.

As an example, let us examine the following chemical reaction:

$$Fe_2O_3\ (s) + 3SO_3\ (\ell) \longrightarrow Fe_2(SO_4)_3\ (s) \qquad \textbf{(2.54)}$$

What is the $\Delta_{rxn}H^\circ$ for this chemical reaction? We can separate this reaction into formation reactions for every reactant and product in the process:

$$Fe_2O_3\ (s) \longrightarrow 2Fe\ (s) + \tfrac{3}{2}O_2\ (g) \qquad \textbf{(a)}$$

$$3[SO_3\ (\ell) \longrightarrow S\ (s) + \tfrac{3}{2}O_2\ (g)] \qquad \textbf{(b)}$$

$$2Fe\ (s) + 3S\ (s) + 6O_2\ (g) \longrightarrow Fe_2(SO_4)_3\ (s) \qquad \textbf{(c)}$$

Reaction a is the reverse reaction for the formation of Fe_2O_3; therefore, the change in enthalpy for a is $-\Delta_f H°$ [Fe_2O_3]. Reaction b is the reverse reaction for the formation of SO_3 (ℓ), and is multiplied by 3. Therefore, the change in enthalpy for b is $-3 \cdot \Delta_f H°$ [SO_3 (ℓ)]. Reaction c is the formation reaction for iron (III) sulfate. The change in enthalpy for c is $\Delta_f H°$ [$Fe_2(SO_4)_3$]. You should verify that the reactions a–c yield equation 2.54 when added together algebraically.

The algebraic combination of the $\Delta_f H°$ values therefore yields the $\Delta_{rxn} H°$ for equation 2.54. We get

$$\Delta_{rxn}H° = -\Delta_f H[Fe_2O_3] - 3 \cdot \Delta_f H[SO_3\ (\ell)] + \Delta_f H[Fe_2(SO_4)_3]$$

Looking up the values in tables shows that $\Delta_f H°$ [Fe_2O_3], $\Delta_f H°$ [SO_3 (ℓ)], and $\Delta_f H°$ [$Fe_2(SO_4)_3$] are -826, -438, and -2583 kJ per mole of compound, respectively. So the $\Delta_{rxn} H°$ for the reaction in equation 2.54 is

$$\Delta_{rxn}H° = -443 \text{ kJ}$$

for the formation of 1 mole of $Fe_2(SO_4)_3$ from Fe_2O_3 and SO_3 at standard pressure.

The above example shows that the $\Delta_f H°$ values of the products are used directly, that the $\Delta_f H°$ values of the reactants have changed sign, and that the coefficients of the balanced chemical reaction are used as multiplicative factors (the multiplier 3 for $\Delta_f H$ for SO_3 and the 3 preceding SO_3 in the balanced chemical reaction is not a coincidence). An understanding of these ideas allows us to develop a short-cut that we can apply to the evaluation of the change in enthalpy for any chemical reaction. (Or any other state function, for that matter, although so far we have internal energy as the only other state function.) For a chemical process,

$$\Delta_{rxn}H = \sum \Delta_f H\,(\text{products}) - \sum \Delta_f H\,(\text{reactants}) \qquad \textbf{(2.55)}$$

In each summation, the number of moles of each product and reactant in the balanced chemical equation must be included. Equation 2.55 applies for any set of conditions, as long as all $\Delta_f H$ values for all species apply to the same conditions. We can also define the change in internal energy for a formation reaction as $\Delta_f U$. This energy change, the internal energy of formation, has a parallel importance to $\Delta_f H$ and is also tabulated. There is also a simple products-minus-reactants expression for the change in internal energy for any chemical process, also based on the $\Delta_f U$ values:

$$\Delta_{rxn}U = \sum \Delta_f U\,(\text{products}) - \sum \Delta_f U\,(\text{reactants}) \qquad \textbf{(2.56)}$$

Again, the general expression applies for both standard and nonstandard conditions, as long as all values apply to the same set of conditions. Appendix 2 contains a large table of (standard) enthalpies of formation. This table should be consulted for problems that require energies of formation reactions. Equations 2.55 and 2.56 eliminate the need to perform a complete Hess's-law type of analysis on every chemical reaction.

Example 2.17

The oxidation of glucose, $C_6H_{12}O_6$, is a basic metabolic process in all life. In cells, it is performed by a complex series of enzyme-catalyzed reactions. The overall reaction is

$$C_6H_{12}O_6\ (s) + 6O_2\ (g) \longrightarrow 6CO_2\ (g) + 6H_2O\ (\ell)$$

If the standard enthalpy of formation of glucose is −1277 kJ/mol, what is the $\Delta_{\text{rxn}}H°$ for this process? You will need to get $\Delta_f H°$ values from Appendix 2.

Solution

The $\Delta_f H$ values for CO_2 (g) and H_2O (ℓ) are −393.51 and −285.83 kJ/mol, respectively. Therefore, we use equation 2.55 and find

$$\Delta_{\text{rxn}}H° = \underbrace{6(-393.51) + 6(-285.83)}_{\Sigma\,\Delta_f H°\,\text{(products)}} - \underbrace{(-1277)}_{\Sigma\,\Delta_f H°\,\text{(reactants)}}\ \text{kJ} \quad \text{for the process}$$

In expressions like these, it is important to keep track of all of the negative signs. Evaluating:

$$\Delta_{\text{rxn}}H° = -2799\ \text{kJ}$$

By noting that the coefficients from the balanced chemical reaction are the number of moles of products and reactants, we lose the moles in the denominator of the $\Delta_{\text{rxn}}H°$. Another way to consider it is to say that 2799 kJ of energy are given off when 1 mole of glucose reacts with 6 moles of oxygen to make 6 moles of carbon dioxide and 6 moles of water. This eliminates the question “moles of what?” that would be raised if a kJ/mol unit were used for $\Delta_{\text{rxn}}H°$.

The products-minus-reactants tactic is a very useful one in thermodynamics. It is also a useful idea to carry along with respect to other state functions: the change in any state function is the final value minus the initial value. In Example 2.17 above, the state function of interest was enthalpy, and by applying Hess’s law and the definition of formation reactions, we were able to develop a procedure for determining the changes in enthalpy and internal energy for a chemical process.

What is the relationship between ΔH and ΔU for a chemical reaction? If one knows the $\Delta_f U$ and $\Delta_f H$ values for the products and reactants, one can simply compare them using the products-minus-reactants scheme of equations 2.55 and 2.56. There is another way to relate these two state functions. Recall the original definition of H from equation 2.16:

$$H = U + pV$$

We also derived an expression for dH as

$$dH = dU + d(pV)$$

$$dH = dU + p\,dV + V\,dp$$

where the second equation above was obtained by applying the chain rule. There are several ways we can go with this. If the chemical process occurs under conditions of constant volume, then the $p\,dV$ term is zero and $dU = dq_V$ (because work = 0). Therefore,

$$dH_V = dq_V + V\,dp \tag{2.57}$$

The integrated form of this equation is

$$\Delta H_V = q_V + V\,\Delta p \tag{2.58}$$

Since $dU = dq$ under constant volume conditions, this gives us one way to calculate how dH differs from dU. Under conditions of constant pressure, the equation becomes

$$\Delta H_p = \Delta U + p\,\Delta V \tag{2.59}$$

and we have a second way of evaluating ΔH and ΔU for a chemical process.

If the chemical process occurs isothermally, then by assuming the gases involved are acting ideally,

$$d(pV) = d(nRT) = dn \cdot RT$$

where dn refers to the change in the number of moles of gas that accompanies the chemical reaction. Since both R and T are constant, the chain rule of calculus does not provide additional terms. Therefore, for isothermal chemical processes, equations 2.58 and 2.59 can be written as

$$\Delta H = \Delta U + RT\,\Delta n \tag{2.60}$$

For equation 2.60, pressure and volume are not constrained to be constant.

Example 2.18

One mole of ethane, C_2H_6, is burned in excess oxygen at constant pressure and 600°C. What is the ΔU of the process? The amount of heat given off by the combustion of 1 mole of ethane is 1560 kJ (that is, it is an exothermic reaction).

Solution

For this constant-pressure process, $\Delta H = q$, so $\Delta H = -1560$ kJ. It is negative because heat is given off. In order to determine $RT\,\Delta n$, we need the balanced chemical reaction. For the combustion of ethane in oxygen, it is

$$C_2H_6\ (g) + \tfrac{7}{2}O_2\ (g) \longrightarrow 2CO_2\ (g) + 3H_2O\ (g)$$

The fractional coefficient is necessary for oxygen in order to balance the reaction. The water product is listed as a gas because the temperature of the process is well above its boiling point! The change in the number of moles of gas, Δn, is $n_{\text{products}} - n_{\text{reactants}} = (2 + 3) - (1 + \frac{7}{2}) = 5 - 4.5 = 0.5$ mole. Therefore,

$$-1560\ \text{kJ} = \Delta U + (0.5\ \text{mol})\left(8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(873\ \text{K})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)$$

Solving:

$$-1560\ \text{kJ} = \Delta U + 1.24\ \text{kJ}$$

$$\Delta U = -1561\ \text{kJ}$$

In this example, $\Delta_{\text{rxn}}U$ and $\Delta_{\text{rxn}}H$ are only slightly different. This shows that *some* of the change in the total energy went into work, and the rest went into heat.

2.11 Changing Temperatures

For a process that occurs under constant pressure (which includes most processes of interest to the chemist), the ΔH of the process is easy to measure. It is equal to the heat, q, of the process. But the temperature of the process can change, and we expect that ΔU and, more importantly, ΔH will vary with the temperature. How do we figure ΔH for a different temperature?

Since enthalpy is a state function, we can select any convenient path to determine ΔH for the reaction at the desired temperature. We can use an idea similar to Hess's law to determine the change in the state function ΔH for a process that occurs at a temperature different from that cited by available data (usually 25.0°C). In addition to ΔH at 25.0°C, we need to know the heat capacities of the products and reactants. Given that information, ΔH_T, where T is any temperature, is given by the sum of:

1. The heat, q, needed to bring the reactants to the temperature specified by the data (usually 298 K)
2. The heat of reaction, ΔH, at that temperature (which can be determined from tabulated data)
3. The heat, q, needed to bring the products *back* to the desired reaction temperature

Using ΔH_1, ΔH_2, and ΔH_3 to label the three heat values listed above, we can write expressions for each step. Step 1 is a change-in-temperature process that uses the fact that $\Delta H_1 = q_p = m \cdot c \cdot \Delta T$. The heat capacity used in this expression is the combined heat capacity of all of the reactants, which must be included stoichiometrically. That is, if there are 2 moles of one reactant, its heat capacity must be included twice, and so on. One must consider whether ΔH_1 represents an exothermic (heat out; ΔH is negative) or an endothermic (heat in; ΔH is positive) change. For step 2, ΔH_2 is simply $\Delta_{\text{rxn}}H°$. For step 3, ΔH_3 is similar to ΔH_1, except that now it is the products that must be taken from the specified temperature to whatever final temperature is necessary (again, keeping track of whether the process is endothermic or exothermic). In this third step, the heat capacities of the *products* are needed. The overall ΔH_T is the sum of the three enthalpy changes, as Hess's law and the fact that enthalpy is a state function require. The following example illustrates.

Example 2.19

Determine ΔH_{500} for the following reaction at 500 K and constant pressure:

$$\text{CO (g)} + \text{H}_2\text{O (g)} \longrightarrow \text{CO}_2\text{ (g)} + \text{H}_2\text{ (g)}$$

The following data are necessary:

Substance	C_p	$\Delta_f H$ (298 K)
CO	29.12	−110.5
H_2O	33.58	−241.8
CO_2	37.11	−393.5
H_2	29.89	0.0

where the units for C_p are J/mol·K and the units for $\Delta_f H$ are kJ/mol. Assume molar quantities.

Solution

First, we have to take CO and H_2O from 500 K to 298 K, a ΔT of −202 K. For one mole of each, the heat (which equals the enthalpy change) is

$$\Delta H_1 = q$$

$$= (1\text{ mol})\left(29.12\ \frac{\text{J}}{\text{mol·K}}\right)(-202\text{ K}) + (1\text{ mol})\left(33.58\ \frac{\text{J}}{\text{mol·K}}\right)(-202\text{ K})$$

$$\Delta H_1 = -12{,}665\text{ J} = -12.665\text{ kJ}$$

For the second step, we need to evaluate ΔH for the reaction at 298 K. Using the products-minus-reactants approach, we find

$$\Delta H_2 = (-393.5 + 0) - (-110.5 + -241.8)\ \text{kJ}$$

$$\Delta H_2 = -41.2\ \text{kJ}$$

Finally, the products of the reaction need to be brought to 500 K; the heat involved in that step, ΔH_3, is

$$\Delta H_3 = q$$

$$= (1\ \text{mol})\left(37.11\ \frac{\text{J}}{\text{mol·K}}\right)(+202\ \text{K}) + (1\ \text{mol})\left(29.89\ \frac{\text{J}}{\text{mol·K}}\right)(+202\ \text{K})$$

where now ΔT is *positive* 202 K:

$$\Delta H_3 = +13{,}534\ \text{J} = 13.534\ \text{kJ}$$

The overall $\Delta_{\text{rxn}}H$ is the sum of the three parts:

$$\Delta_{\text{rxn}}H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$= -12.665 + (-41.2) + 13.534\ \text{kJ}$$

$$\Delta_{\text{rxn}}H = -40.3\ \text{kJ}$$

Figure 2.12 shows a diagram of the processes used to estimate ΔH_{500}.

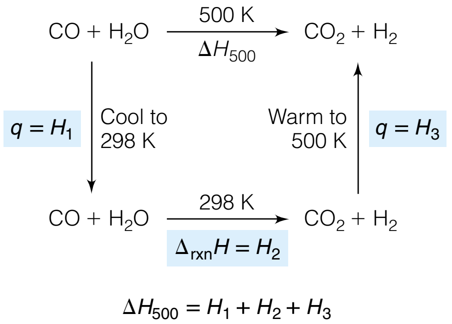

Figure 2.12 A graphical representation of how one determines the $\Delta_{\text{rxn}}H$ at nonstandard temperatures. The total change in enthalpy is the sum of the enthalpy changes for the three steps.

The answer in the above example is not much different from the $\Delta_{\text{rxn}}H°$, but it is different. It is also an approximation, since we are assuming that the heat capacities do not vary with temperature. If one compares this to the experimental value of ΔH_{500} of −39.84 kJ, one sees that we are not far off. It is, then, a good approximation. To be more accurate, an expression for C_p is necessary instead of a constant, and an integral between 500 K and 298 K must be evaluated for the ΔH_1 and ΔH_3 steps, as illustrated in Example 2.10. Conceptually, however, this is no different than the above example.

2.12 Biochemical Reactions

Biology, the study of living things, is based on chemistry. Although biological systems are very complex systems, their chemical reactions are still governed by the basic concepts of thermodynamics. In this section, we review the thermodynamics of some important biochemical processes.

In Example 2.17, we considered the oxidation of glucose:

$$C_6H_{12}O_6\ (s) + 6O_2\ (g) \longrightarrow 6CO_2\ (g) + 6H_2O\ (\ell)$$

The change in enthalpy of this reaction is −2799 kJ per mole of glucose oxidized. The first point to make is that it doesn't matter if the glucose is burned in air or metabolized in our cells: for every 180.15 g (= 1 mol) of glucose that reacts with oxygen, 2799 kJ of energy are given off. The second point is to recognize that this is a lot of energy! It's enough to raise the temperature of 80.0 kg of water (the approximate mass of a human body) by over 8°C! The molar volume of glucose is about 115 mL, illustrating that our cells are using a very compact form of energy.

Photosynthesis is the process by which plants make glucose from carbon dioxide and water. The overall reaction is

$$6CO_2\ (g) + 6H_2O\ (\ell) \longrightarrow C_6H_{12}O_6\ (s) + 6O_2\ (g)$$

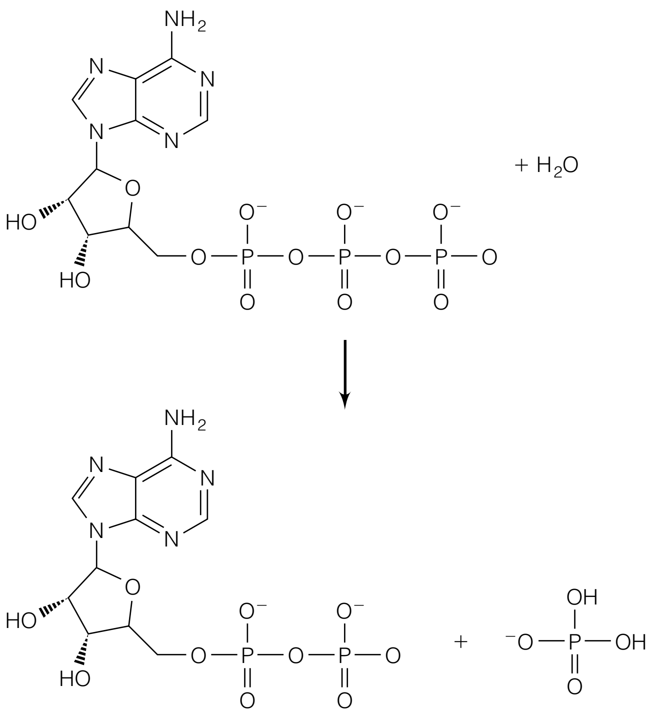

Figure 2.13 Hydrolysis of adenosine triphosphate (ATP) to make adenosine diphosphate (ADP) and inorganic phosphate.

This is the reverse of the reaction for glucose oxidation/metabolism. By Hess's law, the enthalpy change of this reaction is the negative of the enthalpy change for the original process: $\Delta_{\text{rxn}}H = +2799$ kJ per mole of glucose produced. For both processes, the individual steps in the overall, complex biochemical reaction are ignored. Only the overall reaction is needed to determine the enthalpy change.

One very important biochemical reaction is the conversion of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) and vice versa (Figure 2.13). We can summarize this process as

$$\text{ATP} + \text{H}_2\text{O} \rightleftharpoons \text{ADP} + \text{phosphate} \qquad \textbf{(2.61)}$$

Here, "phosphate" refers to any of several inorganic phosphate ions ($H_2PO_4^{\ -}$, $HPO_4^{\ 2-}$, or $PO_4^{\ 3-}$), depending on the ambient conditions. This conversion is a major energy storage/utilization process at the subcellular level.

These reactions occur in cells, not in the gas phase, so the specification of the conditions of the reaction are different. A *biochemical standard state* includes the requirement that an aqueous solution be neutral (that is, neither acidic nor basic), with a pH of 7.* We use the prime symbol ′ on a state function to imply that it refers to a reaction at the biochemical standard state. For the ATP → ADP reaction in equation 2.61, the $\Delta_{\text{rxn}}H^{\circ\prime}$ is −24.3 kJ per mole of ATP reacted.

This is not a large enthalpy change. However, it is enough energy to fuel other biochemically important chemical reactions. Details can be found in most biochemistry textbooks.

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*A more detailed discussion of pH is in Chapter 8.

We end this section with a warning, however. Many biochemistry texts simplify the reaction in equation 2.61 as

$$\text{ATP} \rightleftharpoons \text{ADP} + \text{phosphate} \qquad \Delta_{\text{rxn}}H°' = -24.3 \text{ kJ} \tag{2.62}$$

(It is not uncommon in organic or biological chemistry for complex chemical processes to be written using only the important chemical species.) For the uninitiated, the reaction written in equation 2.62 suggests that an ATP molecule is breaking apart into ADP and phosphate molecules, and 24.3 kJ of energy is given off. However, in basic chemistry we should learn that it always *requires* energy to break a chemical bond; this reaction should be endothermic, not exothermic. How can a chemical bond be broken and energy be given off?

The reason for the confusion is the absence of the H_2O molecule. More bonds are being broken and formed than equation 2.62 implies, and with the inclusion of water (as in equation 2.61), the overall enthalpy change of the ATP → ADP conversion is negative. Confusion arises when complex reactions are simplified and an unsuspecting reader does not recognize the implications of the simplification.

The lesson? Even complex biochemical processes are governed by the concepts of thermodynamics.

2.13 Summary

The first law of thermodynamics concerns *energy.* The total energy of an isolated system is constant. If the total energy of a closed system changes, it can manifest itself as either work or heat, nothing else. Because the internal energy U is not always the best way to keep track of the energy of a system, we define the enthalpy, H, which can be a more convenient state function. Because many chemical processes occur under constant-pressure conditions, enthalpy is often more convenient than internal energy.

There are many mathematical ways of keeping track of the energy changes of a system. The examples we have presented in this chapter are all based on the first law of thermodynamics. Many of them demand a certain condition, like constant pressure, constant volume, or constant temperature. Although this might seem inconvenient, by defining the changes in a system in these ways, we can calculate the change in energy of our system. This is an important goal of thermodynamics. As we will see in the next chapter, it is not the only important goal.

The other task in thermodynamics is embodied in the question "What processes tend to occur by themselves, without any effort (that is, work) on our part?" In other words, what processes are *spontaneous*? Nothing about the first law of thermodynamics helps us answer that question unequivocally. That's because it *can't.* A lot of exploration and experimentation showed that energy is not the only concern of thermodynamics. Other concerns are also important, and it turns out that those concerns play major roles in how we view our universe.

EXERCISES FOR CHAPTER 2

2.2 Work and Heat

2.1. Calculate the work performed by a person who exerts a force of 30 N (N = newtons) to move a box 30 meters if the force were **(a)** exactly parallel to the direction of movement, and **(b)** 45° to the direction of movement. Do the relative magnitudes make sense?

2.2. Explain in your own words why work done by the system is defined as the *negative* of $p\,\Delta V$, not positive $p\,\Delta V$.

2.3. Calculate the work in joules when a piston moves reversibly from a volume of 50. mL to a volume of 450. mL against a pressure of 2.33 atm.

2.4. Calculate the work in joules needed to expand a balloon from 5 mL to 3.350 L against standard atmospheric pressure. (Your lungs provide that work if you are blowing it up yourself.) Assume a reversible process.

2.5. Consider exercise 2.4. Would the work be more or less if it were performed against different external pressures found **(a)** at the top of Mount Everest, **(b)** at the bottom of Death Valley, **(c)** in space? **(d)** What if the process were performed irreversibly?

2.6. Calculate the heat capacity of a material if 288 J of energy were required to heat 50.5 g of the material from 298 K to 330 K. What are the units?

2.7. Liquid hydrogen fluoride, liquid water, and liquid ammonia all have relatively high specific heats for such small molecules. Speculate as to why this might be so.

2.8. A 7.50-g piece of iron at 100.0°C is dropped into 25.0 g of water at 22.0°C. Assuming that the heat lost by the iron equals the heat gained by the water, determine the final temperature of the iron/water system. Assume a heat capacity of water of 4.18 J/g·K and of iron, 0.45 J/g·K.

2.9. With reference to Joule's apparatus in Figure 2.6, assuming a mass of 100. kg of water (about 100 L), a weight with a mass of 20.0 kg, and a drop of 2.00 meters, calculate how many drops it would take to raise the temperature of the water by 1.00°C. The acceleration due to gravity is 9.81 m/s^2. (*Hint:* see Example 2.5.)

2.10. Some people have argued that rocket engines will not work because the gaseous products of a rocket engine, pushing against the vacuum of space, do not perform any work, and therefore the engine will not propel anything. Refute this argument. (*Hint:* consider Newton's third law of motion.)

2.11. Verify equation 2.8.

2.3 Internal Energy; First Law of Thermodynamics

2.12. The statement "Energy can be neither created nor destroyed" is sometimes used as an equivalent statement of the first law of thermodynamics. There are inaccuracies to the statement, however. Restate it to make it less inaccurate.

2.13. Explain why equation 2.10 is not considered a contradiction of equation 2.11.

2.14. What is the change in internal energy when a gas contracts from 377 mL to 119 mL under a pressure of 1550 torr, while at the same time being cooled by removing 124.0 J of heat energy?

2.15. Calculate the work for the isothermal, reversible compression of 0.245 mole of an ideal gas going from 1.000 L to 1 mL if the temperature were 95.0°C.

2.16. Calculate the work done when 1.000 mole of an ideal gas expands reversibly from 1.0 L to 10 L at 298.0 K. Then, calculate the amount of work done when the gas expands irreversibly against a constant external pressure of 1.00 atm. Compare the two values and comment.

2.17. Suppose a change in a gaseous system is adiabatic *and* isothermal. What do you think the change in internal energy would be for such a change?

2.4 & 2.5 State Functions; Enthalpy

2.18. The distance between downtown San Francisco and downtown Oakland is 9 miles. However, a car driving between the two points travels 12.3 miles. Of these distances, which one is analogous to a state function? Why?

2.19. Is temperature a state function? Defend your answer.

2.20. A piston reversibly and adiabatically contracts 3.88 moles of ideal gas to one-tenth of its original volume, then expands back to the original conditions. It does this a total of five times. If the initial and final temperature of the gas is 27.5°C, calculate **(a)** the total work and **(b)** the total ΔU for the overall process.

2.21. Many compressed gases come in large, heavy metal cylinders that are so heavy that they need a special cart to move them around. An 80.0-L tank of nitrogen gas pressurized to 172 atm is left in the sun and heats from its normal temperature of 20.0°C to 140.0°C. Determine **(a)** the final pressure inside the tank and **(b)** the work, heat, and ΔU of the process. Assume that behavior is ideal and the heat capacity of diatomic nitrogen is 21.0 J/mol·K.

2.22. Under what conditions will ΔU be exactly zero for a process whose initial conditions are not the same as its final conditions?

2.23. A balloon filled with 0.505 mole of gas contracts reversibly from 1.0 L to 0.10 L at a constant temperature of 5.0°C. In doing so, it loses 1270 J of heat. Calculate w, q, ΔU, and ΔH for the process.

2.24. It takes 2260 J to vaporize a gram of liquid water to steam at its normal boiling point of 100°C. What is ΔH for this process? What is the work, given that the water vapor expands against a pressure of 0.988 atm? What is ΔU for this process?

2.6 Changes in State Functions

2.25. If the infinitesimals of internal energy were taken with respect to pressure and volume, what would be the equation for the infinitesimal change in internal energy dU? Write a similar expression for dH, assuming the same variables.

2.26. A refrigerator contains approximately 17 cubic feet, or about 480 liters, of air. Assuming it acts as an ideal gas with a $\overline{C}_V$ of 12.47 J/mol·K, what is the change in U in cooling the air from normal room temperature (22°C) to refrigerator temperature (4°C)? Assume an initial pressure of 1.00 atm.

2.27. What are the units on each term of the equation for C_V given in part b of Example 2.10?

2.28. Starting with equation 2.27 and the original definition of enthalpy, derive the fact that $\overline{C}_p = \overline{C}_V + R$.

2.29. Derive the fact that $(\partial H/\partial p)_T$ is also zero for an ideal gas.

2.30. Define isobaric, isochoric, isenthalpic, and isothermal. Can a change in a gaseous system be isobaric, isochoric, and isothermic at the same time? Why or why not?

2.7 Joule-Thomson Coefficients

2.31. Starting from the cyclic rule involving the Joule-Thomson coefficient, derive equation 2.35.

2.32. The ideal gas law is the equation of state for an ideal gas. Why can't it be used to determine $(\partial T/\partial p)_H$?

2.33. For a gas that follows the van der Waals equation of state, the inversion temperature can be approximated as $2a/Rb$. Using Table 1.6, calculate the inversion temperatures of He and H_2 and compare them to their values of 40 K and 202 K, respectively. What are the implications of these inversion temperatures with regard to liquefaction of these two gases?

2.34. Estimate the final temperature of a mole of gas at 200.00 atm and 19.0°C as it is forced through a porous plug to a final pressure of 0.95 atm. The μ_{JT} of the gas is 0.150 K/atm.

2.35. With regard to exercise 2.34, how accurate do you think your answer is, and why?

2.36. Someone proposes that the Joule-Thomson coefficient can also be defined as

$$\mu_{JT} = -\frac{(\partial U/\partial p)_T}{C_V}$$

Is this definition valid? Why or why not?

2.8 Heat Capacities

2.37. Why is equation 2.37 written in terms of C_V and C_p and not $\overline{C}_V$ and $\overline{C}_p$?

2.38. What are the numerical values of the heat capacities $\overline{C}_p$ and $\overline{C}_V$ of a monatomic ideal gas, in units of cal/mol·K and L·atm/mol·K?

2.39. In a constant-pressure calorimeter (that is, one that expands or contracts if the volume of the system changes), 0.145 mol of an ideal gas contracts slowly from 5.00 L to 3.92 L. If the initial temperature of the gas is 0.0°C, calculate the ΔU and w for the process.

2.40. What is the final temperature of 0.122 mole of ideal gas that performs 75 J of work adiabatically if the initial temperature is 235°C?

2.41. Derive equation 2.44 from the previous step.

2.42. Show that $(\overline{C}_p - \overline{C}_V)/\overline{C}_V$ equals $\frac{2}{3}$ for a monatomic ideal gas.

2.43. What is γ for an ideal diatomic gas? (See footnote in section 2.8.)

2.44. In orbit about Earth, a weather balloon jettisons a weight and ascends to a higher altitude. If the initial pressure inside the balloon is 0.0033 atm and it ascends to an altitude where the pressure is 0.00074 atm, by what fraction does the absolute temperature change? Assume that the balloon is filled with helium, a good approximation of an ideal gas, and that the change is adiabatic.

2.9 & 2.10 Phase and Chemical Changes

2.45. Take the volume change into account and calculate ΔH and ΔU for exactly 1 g of ice melting into 1 g of water at standard pressure. The density of ice at 0° is 0.9168 g/mL; the density of water at 0° is 0.99984 g/mL.

2.46. How much work is performed by 1 mole of water freezing to 1 mole of ice at 0°C at standard pressure? Use the densities from the previous exercise.

2.47. Why are steam burns so much worse than water burns even if the H_2O is at the same temperature for both phases? (*Hint:* consider the heat of vaporization of water.)

2.48. How many grams of water at 0°C will be melted by the condensation of 1 g of steam at 100°C?

2.49. Citrus farmers sometimes spray their trees with water if the temperature is expected to go below 32°F, in the hopes that this will keep the fruit from freezing. Why would farmers think that?

2.50. Draw a diagram like Figure 2.11 that illustrates the change in enthalpy for the chemical reaction

$$C\ (s) + 2H_2\ (g) \longrightarrow CH_4\ (g)$$

which is exothermic by 74.8 kJ/mol.

2.51. Determine the $\Delta_{rxn}H$ (25°C) of the following reaction:

$$H_2\ (g) + I_2\ (s) \longrightarrow 2HI\ (g)$$

2.52. Determine $\Delta_{rxn}H$ (25°C) for the following reaction:

$$NO\ (g) + \tfrac{1}{2}O_2\ (g) \longrightarrow NO_2\ (g)$$

This reaction is a major participant in the formation of smog.

2.53. Using Hess's law, write out all of the formation reactions that add up to, and calculate $\Delta_{rxn}H$ (25°C) for, the following reaction:

$$2NaHCO_3\ (s) \longrightarrow Na_2CO_3\ (s) + CO_2\ (g) + H_2O\ (\ell)$$

(This reaction occurs when one uses baking soda to smother a fire in the kitchen.)

2.54. The thermite reaction combines aluminum powder and iron oxide and ignites the mixture to make aluminum oxide and iron. So much energy is given off that the iron product frequently is molten. Write a balanced chemical reaction for the thermite process and determine its ΔH (25°C) .

2.55. Benzoic acid, C_6H_5COOH, is a common standard used in bomb calorimeters, which maintain a constant volume. If 1.20 g of benzoic acid gives off 31,723 J of energy when burned in the presence of excess oxygen at a constant temperature of 24.6°C, calculate q, w, ΔH, and ΔU for the reaction.

2.56. 1.20 g of benzoic acid, C_6H_5COOH, is burned in a porcelain dish exposed to the air. If 31,723 J of energy is given off and the system temperature is 24.6°C, calculate q, w, ΔH, and ΔU. (Compare your answers to those from the previous problem.)

2.11 Changing Temperatures

2.57. Assuming constant heat capacities for products and reactants, determine the ΔH (500°C) for $2H_2\text{ (g)} + O_2\text{ (g)} \rightarrow 2H_2O\text{ (g)}$. (*Hint:* be careful which data you use for water!)

2.58. Use the heat capacities of the products and reactants of the thermite reaction and the calculated ΔH of the process to estimate the temperature of the reaction. Assume that all of the heat generated goes to increasing the temperature of the system.

Symbolic Math Exercises

2.59. The following are values of heat capacity for nitrogen gas:

Temp (K)	C_V (J/mol·K)
300	20.8
400	20.9
500	21.2
600	21.8
700	22.4
800	23.1
900	23.7
1000	24.3
1100	24.9

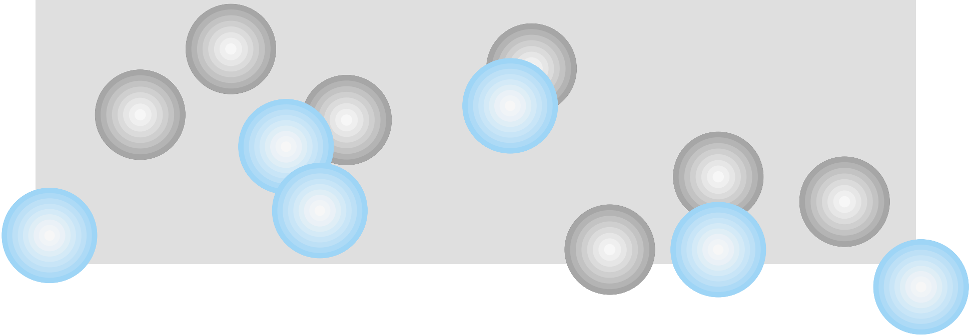
Using the general formula $C_V = A + BT + C/T^2$, find values of A, B, and C that fit the given data.

2.60. What is ΔU for 1 mole of N_2 gas going from 300 K to 1100 K at constant volume? Use the expression for C_V you determined from exercise 2.59, and evaluate ΔU numerically.

2.61. Consider a gas undergoing a reversible, adiabatic change in volume. Such changes are not isothermal, but you can still use the special case of Boyle's law in equation 2.49. Plot the final pressure of 1.00 mole of ideal gas at 1.00 bar initial pressure as the volume increases. Also plot the isothermal final pressure as volume increases from the same initial conditions (that is, Boyle's law). How do these two plots compare?

3

The Second and Third Laws of Thermodynamics



ALTHOUGH THE MATHEMATICAL AND CONCEPTUAL TOOLS PROVIDED BY THE ZEROTH AND FIRST LAWS OF THERMODYNAMICS ARE VERY USEFUL, we need more. There is a major question that these laws cannot answer: Will a given process occur spontaneously? Nothing in the previous chapters addresses spontaneity, which is an important concept. Thermodynamics helps to understand the spontaneity of processes—but only once we add more of its tools. These tools are called the second and third laws of thermodynamics.

3.1 Synopsis

As useful as the first law of thermodynamics is, we will see that it is limited. There are some questions that it cannot answer. First, we will consider some of the limitations of the first law. We will then introduce efficiency and see how it applies to engines, which are devices that convert heat into work. The second law of thermodynamics can be expressed in terms of efficiency, so we will introduce the second law at this point.

Our treatment of engines will suggest a new state function, called entropy. Using its initial definition as a start, we will derive some equations that allow us to calculate the entropy changes for various processes. After considering a different way of defining entropy, we will state the third law of thermodynamics, which makes entropy a unique state function in thermodynamics. Finally, we will consider entropy changes for chemical reactions.

In this chapter, we focus almost exclusively on the entropy of the system, not the surroundings. Most processes of interest to us involve some sort of interaction between the system and the surroundings, but the system itself remains the part of the universe of interest to us.

3.2 Limits of the First Law

Will a chemical or physical process occur spontaneously? A process occurring inside a system is *spontaneous* if the surroundings are not required to perform work on the system. For example, if you drop a rock from a waist-high height, the rock will fall spontaneously. When the plunger of a spray can of hair spray is pressed, gas comes out spontaneously. When metallic sodium is placed in a jar filled with chlorine gas, a chemical reaction occurs spontaneously, making sodium chloride as a product.

However, a rock on the ground does not jump up to waist height spontaneously. Hair spray does not spontaneously rush back into the can at high pressure, and sodium chloride does not spontaneously react into metallic sodium and diatomic chlorine gas. These are examples of *nonspontaneous* changes. These changes can be made to occur, by performing some sort of work. For example, sodium chloride can be melted and an electric current run through it, generating sodium and chlorine, but in such a case we are forcing a nonspontaneous process to occur. The process is not occurring on its own. As a final example, consider the isothermal, adiabatic free expansion of an ideal gas. The process is spontaneous, but it occurs with no change in energy of the gas in the system.

How can we predict which processes are spontaneous? Consider the three cases used above. When a rock falls, it goes to a lower gravitational potential energy. When high-pressure gas goes to a lower pressure, it occurs with a decrease in energy. When sodium and chlorine react, the exothermic reaction means that energy is given off and the overall system has gone to a lower energy. We therefore make the following suggestion: spontaneous processes occur if the energy of the system decreases. Is this a sufficient definition and an able predictor of a spontaneous process? Is this general statement universally applicable to all spontaneous processes?

Consider the following process:

$$\text{NaCl (s)} \xrightarrow{\text{H}_2\text{O}} \text{Na}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$$

which is the dissolution of sodium chloride in water. The change in enthalpy for this process is an example of a *heat of solution,* $\Delta_{\text{soln}}H$. This particular process, which occurs spontaneously (since sodium salts are soluble), has a $\Delta_{\text{soln}}H$ (25°C) of $+3.88$ kJ/mol. It is an *endothermic* process, yet it occurs spontaneously. Consider the chemical reaction of a common chemical demonstration:

$$\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O (s)} + 2\text{NH}_4\text{SCN (s)} \longrightarrow \text{Ba(SCN)}_2 \text{ (s)} + 2\text{NH}_3 \text{ (g)} + 10\text{H}_2\text{O } (\ell)$$

This reaction absorbs so much energy from the surroundings (that is, it is so endothermic) that it can freeze water into ice, which is the major point of the demonstration. The system (that is, the chemical reaction) is increasing in energy, but it too is spontaneous.

The conclusion is that a decrease in the energy of a system is insufficient in itself to predict whether a process in that system will be spontaneous. Most spontaneous changes, but not all, are accompanied by a decrease in energy. Therefore, a decrease in energy for a change is not sufficient to determine whether or not the change is spontaneous.

Unfortunately, the first law of thermodynamics deals with *changes in energy* only. But we have seen that consideration of energy changes alone is insufficient for determining whether or not changes in the system are spontaneous. Does this mean that the first law of thermodynamics is wrong? No! It only means that the first law *alone* cannot address this particular question.

Thermodynamics does provide other tools with which to study processes. The consideration of these tools not only broadens the applicability of thermodynamics, but goes a long way toward answering the question, "Is this process spontaneous?" We will introduce and develop the tools in this chapter, and consider a very specific answer to the question in the next chapter.

3.3 The Carnot Cycle and Efficiency

In 1824, a French military engineer named Nicolas Leonard Sadi Carnot (his third name is borrowed from a Persian poet, and his surname is pronounced kar-NO) published an article that ultimately played a major—though roundabout—role in the development of thermodynamics. It was ignored at the time. The first law of thermodynamics had not even been established yet, and heat was still thought of as "caloric." It was not until 1848 that Lord Kelvin brought the attention of the scientific world to the work, 16 years after Carnot's early death at age 36. However, the article introduced a lasting concept, the definition of the Carnot cycle.

Carnot was interested in understanding the ability of steam engines—known for almost a century by that time—to perform work. He was apparently the first to understand that there was a relationship between the *efficiency* of a steam engine and the *temperatures* involved in the process. Figure 3.1 shows a modern diagram of how Carnot defined an engine. Carnot realized that every engine could be defined as getting heat, q_{in}, from some high-temperature reservoir. The engine performed some work, w, on the surroundings. The engine then disposed of the leftover heat in a reservoir that has some lower temperature. The engine is therefore emitting some heat, q_{out}, into the low-temperature reservoir. Although the engines of today are much different from those of Carnot's time, every device we have for performing work can be modeled in this fashion.

Carnot proceeded to define the steps for the operation of an engine in such a way that the maximum efficiency could be achieved. These steps, collectively called the *Carnot cycle,* represent the most efficient way known to get work out of heat, as energy goes from a high-temperature reservoir to a low-temperature reservoir. The engine itself is defined as the system, and a schematic of the

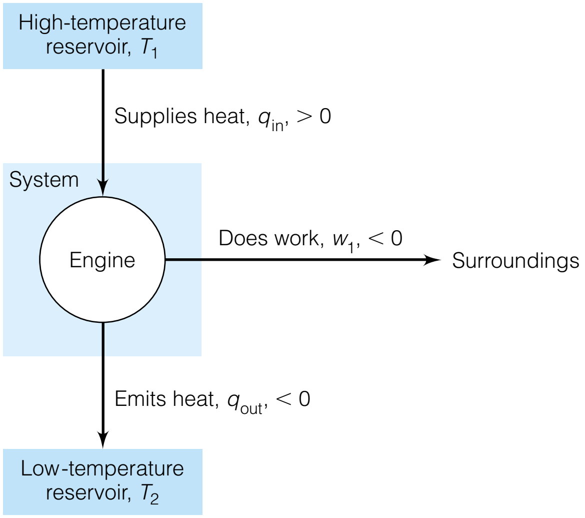


Figure 3.1 A modern diagram of the type of engine that Carnot considered for his cycle. The high-temperature reservoir supplies the energy to run the engine, which produces some work and emits the remainder of the energy into a low-temperature reservoir. The values of q_{in}, w_1, and q_{out} are greater or less than zero with respect to the *system.*

cycle is shown in Figure 3.2. The steps of a Carnot cycle are, for an ideal gaseous system:

1. Reversible isothermal expansion. In order for this to occur, heat must be absorbed from the high-temperature reservoir. We shall define this amount of heat as q_1 (labeled as q_{in} in Figure 3.1) and the amount of work performed by the system as w_1.
2. Reversible adiabatic expansion. In this step, $q = 0$, but since it is expansion, work is done by the engine. The work is defined as w_2.
3. Reversible isothermal compression. In order for this step to be isothermal, heat must leave the system. It goes into the low-temperature reservoir and will be labeled q_3 (this is labeled as q_{out} in Figure 3.1). The amount of work in this step will be called w_3.
4. Reversible adiabatic compression. The system (that is, the engine) is returned to its original conditions. In this step, q is 0 again, and work is done on the system. This amount of work is termed w_4.

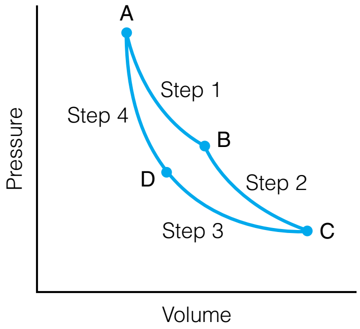


Figure 3.2 A representation of the Carnot cycle performed on a gaseous system. The steps are: (1) Reversible isothermal expansion. (2) Reversible adiabatic expansion. (3) Reversible isothermal compression. (4) Reversible adiabatic compression. The system ends up at the same conditions it started at; the volume inside the four-sided figure is representative of the $p - V$ work performed by the cycle.

Since the system has returned to the original conditions, by definition of a state function, $\Delta U = 0$ for the overall process. By the first law of thermodynamics,

$$\Delta U = 0 = q_1 + w_1 + w_2 + q_3 + w_3 + w_4 \tag{3.1}$$

Another way of writing this is to consider the entire work performed by the cycle, as well as the entire heat flow of the cycle:

$$w_{\text{cycle}} = w_1 + w_2 + w_3 + w_4 \tag{3.2}$$

$$q_{\text{cycle}} = q_1 + q_3 \tag{3.3}$$

so that

$$0 = q_{\text{cycle}} + w_{\text{cycle}}$$

$$q_{\text{cycle}} = -w_{\text{cycle}} \tag{3.4}$$

We now define *efficiency* e as the negative ratio of the work of the cycle to the heat that comes from the high-temperature reservoir:

$$e = -\frac{w_{\text{cycle}}}{q_1} \tag{3.5}$$

Efficiency is thus a measure of how much heat going into the engine has been converted into work. The negative sign makes efficiency positive, since work done *by* the system has a negative value but heat coming *into* the system has a positive value. We can eliminate the negative sign by substituting for w_{cycle} from equation 3.4:

$$e = \frac{q_{\text{cycle}}}{q_1} = \frac{q_1 + q_3}{q_1} = 1 + \frac{q_3}{q_1} \tag{3.6}$$

Since q_1 is heat going into the system, it is positive. Since q_3 is heat going out of the system (into the low-temperature reservoir of Figure 3.1), it is negative. Therefore, the fraction q_3/q_1 will be negative. Further, it can be argued that the heat leaving the engine will never be greater than the heat entering the engine. That would violate the first law of thermodynamics, that energy cannot be created. Therefore the magnitude $|q_3/q_1|$ will never be greater than 1, but it will always be less than or (if no work is done) equal to 1. Combining all these statements, we conclude that

The efficiency of an engine will always be between 0 and 1.

Example 3.1

a. Determine the efficiency of a Carnot engine that takes in 855 J of heat, performs 225 J of work, and gives off the remaining energy as heat.
b. Draw a diagram like Figure 3.1 showing the exact amounts of heat and work going from place to place in the proper direction.

Solution

a. Using both definitions of efficiency, and recognizing the proper signs on the heat and work:

$$e = -\frac{-225\ \mathrm{J}}{+855\ \mathrm{J}} = 0.263$$

$$e = 1 + \frac{-(855 - 225)\ \mathrm{J}}{855\ \mathrm{J}} = 1 + (-0.737) = 0.263$$

b. The drawing is left to the student.

There is another way to define efficiency in terms of the temperatures of the high- and low-temperature reservoirs. For the isothermal steps 1 and 3, the change in the internal energy is zero because $(\partial U/\partial V)_T = 0$. Therefore, $q = -w$ for steps 1 and 3. From equation 2.7, for an ideal gas,

$$w = -nRT \ln \frac{V_\mathrm{f}}{V_\mathrm{i}}$$

For a reversible, isothermal process, the heats for steps 1 and 3 are

$$q_1 = -w_1 = nRT_\mathrm{high} \ln \frac{V_\mathrm{B}}{V_\mathrm{A}} \qquad \textbf{(3.7)}$$

$$q_3 = -w_3 = nRT_\mathrm{low} \ln \frac{V_\mathrm{D}}{V_\mathrm{C}} \qquad \textbf{(3.8)}$$

The volume labels A, B, C, and D represent the initial and final points for each step, as shown in Figure 3.2. T_high and T_low are the temperatures of the high-temperature and low-temperature reservoirs, respectively. For the adiabatic steps 2 and 4, we can use equation 2.47 to get

$$\left(\frac{V_\mathrm{B}}{V_\mathrm{C}}\right)^{2/3} = \frac{T_\mathrm{low}}{T_\mathrm{high}}$$

$$\left(\frac{V_\mathrm{A}}{V_\mathrm{D}}\right)^{2/3} = \frac{T_\mathrm{low}}{T_\mathrm{high}}$$

Equating the two volume expressions, which both equal $T_\mathrm{low}/T_\mathrm{high}$:

$$\left(\frac{V_\mathrm{A}}{V_\mathrm{D}}\right)^{2/3} = \left(\frac{V_\mathrm{B}}{V_\mathrm{C}}\right)^{2/3}$$

Raising both sides to the power of 3/2 and rearranging, we get

$$\left(\frac{V_\mathrm{A}}{V_\mathrm{B}}\right) = \left(\frac{V_\mathrm{D}}{V_\mathrm{C}}\right)$$

Substituting for $V_\mathrm{D}/V_\mathrm{C}$ in equation 3.8, we get an expression for q_3 in terms of volumes V_A and V_B:

$$q_3 = nRT_\mathrm{low} \ln \frac{V_\mathrm{A}}{V_\mathrm{B}} = -nRT_\mathrm{low} \ln \frac{V_\mathrm{B}}{V_\mathrm{A}} \qquad \textbf{(3.9)}$$

Equations 3.7 and 3.9 can be divided to get a new expression for the ratio q_3/q_1:

$$\frac{q_3}{q_1} = \frac{nRT_{\text{low}} \ln \dfrac{V_\text{B}}{V_\text{A}}}{-nRT_{\text{high}} \ln \dfrac{V_\text{B}}{V_\text{A}}} = -\frac{T_{\text{low}}}{T_{\text{high}}}$$

Substituting into equation 3.6, we get an equation for efficiency in terms of the temperatures:

$$e = 1 - \frac{T_{\text{low}}}{T_{\text{high}}} \tag{3.10}$$

Equation 3.10 has some interesting interpretations. First, the efficiency of an engine is very simply related to the *ratio* of the low- and high-temperature reservoirs. The smaller this ratio is, the more efficient an engine is.* Thus, high efficiencies are favored by high T_{high} values and low T_{low} values. Second, equation 3.10 allows us to describe a *thermodynamic* scale for temperature. It is a scale for which $T = 0$ when the efficiency equals 1 for the Carnot cycle. This scale is the same one used for ideal gas laws, but it is based on the efficiency of a Carnot cycle, rather than the behavior of ideal gases.

Finally, unless the temperature of the low-temperature reservoir is absolute zero, the efficiency of an engine will never be 1; it will always be less than 1. Since it can be shown that absolute zero is physically unobtainable for a macroscopic object, we have the further statement that

No engine can ever be 100% efficient.

When one generalizes by recognizing that every process can be considered an engine of some sort, the statement becomes

No process can ever be 100% efficient.

It is statements like this that preclude the existence of perpetual motion machines, devices that purportedly have an efficiency greater than 1 (that is, $>$100%), producing more work out than the energy coming in. Carnot's study of steam engines helped establish such statements, and so much faith is placed in them that the U.S. Patent Office categorically does not consider any patent application claiming to be a perpetual motion machine (although some applications for such machines are considered because they disguise themselves to cover the fact). Such is the power of the laws of thermodynamics.

The two definitions of efficiency can be combined:

$$1 + \frac{q_3}{q_1} = 1 - \frac{T_{\text{low}}}{T_{\text{high}}}$$

$$\frac{q_3}{q_1} = -\frac{T_{\text{low}}}{T_{\text{high}}}$$

$$\frac{q_3}{q_1} + \frac{T_{\text{low}}}{T_{\text{high}}} = 0$$

$$\frac{q_3}{T_{\text{low}}} + \frac{q_1}{T_{\text{high}}} = 0 \tag{3.11}$$

Notice that q_3 is the heat that goes to the low-temperature reservoir, whereas q_1 is the heat that comes from the high-temperature reservoir. Each fraction

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*In practice, other factors (including mechanical ones) reduce the efficiency of most engines.

therefore contains heats and temperatures from related parts of the universe under consideration. Note that equation 3.11 includes *all* of the heats of the Carnot cycle. The fact that these heats, divided by the absolute temperatures of the two reservoirs involved, add up to exactly zero is interesting. Recall that the cycle starts and stops at the same system conditions. But changes in state functions are dictated solely by the conditions of the system, not by the path that got the system to those conditions. If a system starts and stops at the same conditions, overall changes in state functions are exactly zero. Equation 3.11 suggests that *for reversible changes, a relationship between heat and absolute temperature is a state function.*

3.4 Entropy and the Second Law of Thermodynamics

We define *entropy, S*, as an additional thermodynamic state function. The infinitesimal change in entropy, dS, is defined as

$$dS = \frac{dq_{\text{rev}}}{T} \tag{3.12}$$

where "rev" on the infinitesimal for heat, dq, specifies that it must be the heat for a reversible process. The temperature, T, must be in kelvins. Integrating equation 3.12, we get

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} \tag{3.13}$$

where ΔS is now the change in entropy for a process. As indicated in the previous section, for the Carnot cycle (or any other closed cycle) ΔS must be zero.

For an *isothermal, reversible process,* the temperature can be taken out of the integral and the integral can be evaluated easily:

$$\Delta S = \frac{1}{T}\int dq_{\text{rev}} = \frac{q_{\text{rev}}}{T} \tag{3.14}$$

Equation 3.14 demonstrates that entropy has units of J/K. These may seem like unusual units, but they are the correct ones. Also, keep in mind that the amount of heat for a process depends on the amount of material, in grams or moles, and so sometimes the unit for entropy becomes J/mol·K. Example 3.2 shows how to include amount in the unit.

Example 3.2

What is the change in entropy when 1.00 g of benzene, C_6H_6, boils reversibly at its boiling point of 80.1°C and a constant pressure of 1.00 atm? The heat of vaporization of benzene is 395 J/g.

Solution

Since the process occurs at constant pressure, $\Delta_{\text{vap}}H$ for the process equals the heat, q, for the process. Since vaporization is an endothermic (that is, energy-in) process, the value for the heat is positive. Finally, 80.1°C equals 353.2 K. Using equation 3.14:

$$\Delta S = \frac{+395\ \text{J}}{353.2\ \text{K}} = +1.12\ \frac{\text{J}}{\text{K}}$$

for 1 g of benzene. Since this represents the entropy change for 1 g of benzene, we can also write this ΔS as $+1.12$ J/g·K. The entropy of the system—the benzene—is increasing in this example.

Other cyclic processes having different steps or conditions can be defined. However, it has been found that no known process is more efficient than a Carnot cycle, which is defined in terms of *reversible* steps. This means that any irreversible change is a less efficient conversion of heat to work than a reversible change, since a Carnot cycle is defined in terms of reversible processes. So, for any arbitrary process:

$$e_{\mathrm{arb}} \leq e_{\mathrm{Carnot}}$$

where e_{arb} is the efficiency for that arbitrary cycle and e_{Carnot} is the efficiency of a Carnot cycle. If the arbitrary process is a Carnot-type cycle, then the "equals" part of the sign applies. If the cycle is an irreversible cycle, the "less than" part of the sign applies. Substituting for efficiency:

$$1 + \frac{q_{\mathrm{out,arb}}}{q_{\mathrm{in,arb}}} \leq 1 + \frac{q_{3,\mathrm{Carnot}}}{q_{1,\mathrm{Carnot}}}$$

$$\frac{q_{\mathrm{out,arb}}}{q_{\mathrm{in,arb}}} \leq \frac{q_{3,\mathrm{Carnot}}}{q_{1,\mathrm{Carnot}}}$$

where the 1s have canceled. The fraction on the right is equal to $-T_{\mathrm{low}}/T_{\mathrm{high}}$, as demonstrated earlier. Substituting:

$$\frac{q_{\mathrm{out,arb}}}{q_{\mathrm{in,arb}}} \leq -\frac{T_{\mathrm{low}}}{T_{\mathrm{high}}}$$

and rearranging:

$$\frac{q_{\mathrm{out,arb}}}{q_{\mathrm{in,arb}}} + \frac{T_{\mathrm{low}}}{T_{\mathrm{high}}} \leq 0$$

This equation can be rearranged to get the heat and temperature variables that are associated with the two reservoirs into the same fractions (that is, q_{in} with T_{high} and q_{out} with T_{low}). It is also convenient to relabel the temperatures and/or the heats to emphasize which steps of the Carnot cycle are involved. Finally, we will drop the "arb" designation. (Can you reproduce these steps?) The above expression thus simplifies to

$$\frac{q_3}{T_3} + \frac{q_1}{T_1} \leq 0$$

For the complete cycle of many steps, we can write this as a summation:

$$\sum_{\text{all steps}} \frac{q_{\mathrm{step}}}{T_{\mathrm{step}}} \leq 0$$

As each step gets smaller and smaller, the summation sign can be replaced by an integral sign, and the above expression becomes

$$\int \frac{dq}{T} \leq 0 \tag{3.15}$$

for any complete cycle. Equation 3.15 is one way of stating what is called Clausius's theorem, after Rudolf Julius Emmanuel Clausius, a Pomeranian (now part of Poland) and German physicist who first demonstrated this relationship in 1865.

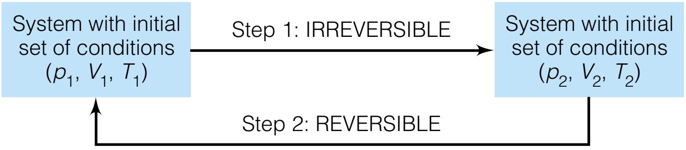

Figure 3.3 A representation of a process that has an irreversible step. See text for discussion. Most real processes can be described like this, giving entropy a meaningful place in the understanding of real processes.

Consider, then, the two-step process illustrated in Figure 3.3, where an irreversible step takes a system from a set 1 of conditions to a set 2 of conditions, and then a reversible step takes it back to the original conditions. As a state function, the sum of the steps equals the overall change for the entire process. But from equation 3.15, the overall integral's value must be less than zero. Separating the integral into two parts:

$$\int_1^2 \frac{dq_{\text{irrev}}}{T} + \int_2^1 \frac{dq_{\text{rev}}}{T} < 0$$

The expression inside the second integral is, by the definition in equation 3.12, *dS*. If we reverse the limits on the second integral (so both terms refer to the same process going in the same, not opposite, directions), it becomes $-dS$. We therefore have

$$\int_1^2 \frac{dq_{\text{irrev}}}{T} + \int_1^2 (-dS) < 0$$

or

$$\int_1^2 \frac{dq_{\text{irrev}}}{T} - \int_1^2 dS < 0$$

The integral of *dS* is ΔS, so for this step we have

$$\int_1^2 \frac{dq_{\text{irrev}}}{T} - \Delta S < 0$$

$$\int_1^2 \frac{dq_{\text{irrev}}}{T} < \Delta S$$

Reversing and generalizing for any step, we simply remove the specific limits:

$$\Delta S > \int \frac{dq_{\text{irrev}}}{T} \tag{3.16}$$

If we want to keep this in terms of infinitesimals (that is, without integral signs) as well as include the original definition of *dS* from equation 3.12, this becomes

$$dS \geq \frac{dq}{T} \tag{3.17}$$

where again the equality is applicable to reversible processes, and the inequality is applicable to irreversible processes.

But consider that a spontaneous process *is* an irreversible process. Spontaneous processes will occur if they can. With that in mind, we have the following generalizations:

$$dS > \frac{dq}{T} \quad \text{for irreversible, spontaneous processes}$$

$$dS = \frac{dq}{T} \quad \text{for reversible processes}$$

Equation 3.17 also implies

$$dS < \frac{dq}{T} \quad \text{not allowed}$$

The last statement is particularly important: the infinitesimal change in S will not be less than dq/T. It may be equal to or greater than dq/T, but *it will not be less than that.*

Consider, then, the following description. A process occurs in an isolated system. Under what conditions will the process occur? If the system is truly isolated (there is no transfer of energy or matter between system and surroundings), then the process is adiabatic, since isolation implies that $q = 0$, and by extension $dq = 0$. Therefore, dq/T is equal to zero. We can therefore revise the above statements:

$dS > 0$ if the process is irreversible and spontaneous

$dS = 0$ if the process is reversible

$dS < 0$ is not allowed for a process in an isolated system

We conceptually collect the above three statements into one, which is the second law of thermodynamics:

> The second law of thermodynamics: For an isolated system, if a spontaneous change occurs, it occurs with a concurrent increase in the entropy of the system.

If a spontaneous change does occur, entropy is the sole driving force for that change because both q and w are zero—and therefore ΔU is zero—under the stated conditions.

3.5 More on Entropy

In Example 3.2, we calculated the entropy change for an isothermal process. What if the process were not isothermal? For a given mass

$$dq = C\,dT$$

where C is the heat capacity, we can substitute for dq in the infinitesimal change in entropy:

$$dS = \frac{dq_{\text{rev}}}{T} = \frac{C\,dT}{T}$$

and then integrate:

$$\Delta S = \int dS = \int \frac{C\,dT}{T} = C \int \frac{dT}{T} = C \ln T\Big|_{T_\text{i}}^{T_\text{f}}$$

for a constant heat capacity. Evaluating at the temperature limits and using the properties of logarithms:

$$\Delta S = C \ln \frac{T_\text{f}}{T_\text{i}} \tag{3.18}$$

For n moles, this equation becomes $\Delta S = n\overline{C} \ln(T_\text{f}/T_\text{i})$ and $\overline{C}$ will have units of J/mol·K. If C has units of J/g·K, then the mass of the system is necessary. If the heat capacity is not constant over the specified temperature range, then the temperature-dependent expression for C must be included explicitly inside the integral and the function must be evaluated on a term-by-term basis.

Fortunately, most expressions for heat capacity are simple power series in T, whose integrals are easy to evaluate on a term-by-term basis.

There is no V or p subscript on the symbol for the heat capacity in equation 3.18. That's because it depends on the conditions of the process. If it occurs under conditions of constant volume, use C_V. If it occurs under conditions of constant pressure, use C_p. Usually the particular process involved dictates the choice.

Now consider gas-phase processes. What if the temperature were constant but the pressure or the volume changed? If the gas is ideal, ΔU for the process is exactly zero, so $dq = -dw = +p\, dV$. Substituting again for dq, then:

$$dS = \frac{dq}{T} = \frac{p\, dV}{T}$$

$$\Delta S = \int dS = \int \frac{p\, dV}{T}$$

At this point, we can substitute for either p or dV using the ideal gas law. If we substitute for p in terms of V (that is, $p = nRT/V$):

$$\Delta S = \int \frac{nRT\, dV}{VT} = \int \frac{nR\, dV}{V} = nR \int \frac{dV}{V}$$

$$\Delta S = nR \ln \frac{V_\mathrm{f}}{V_\mathrm{i}} \tag{3.19}$$

Similarly, for a change in pressure one gets:

$$\Delta S = -nR \ln \frac{p_\mathrm{f}}{p_\mathrm{i}} \tag{3.20}$$

Because entropy is a state function, the change in entropy is dictated by the conditions of the system, not how the system arrived at those conditions. Therefore, any process can usually be broken down into smaller steps, the entropy of each step can be evaluated using the growing number of expressions for ΔS, and the ΔS for the overall process is the combination of all of the ΔS's of the individual steps.

Example 3.3

Determine the overall change in entropy for the following process using 1.00 mole of He:

$$\text{He (298.0 K, 1.50 atm)} \longrightarrow \text{He (100.0 K, 15.0 atm)}$$

The heat capacity of He is 20.78 J/mol·K. Assume the helium acts ideally.

Solution

The overall reaction can be divided into two parts:

Step 1: He (298.0 K, 1.50 atm) → He (298.0 K, 15.0 atm)
(change in pressure step)
Step 2: He (298.0 K, 15.0 atm) → He (100.0 K, 15.0 atm)
(change in temperature step)

The change in entropy for step 1, the isothermal step, can be determined from equation 3.20:

$$\Delta S_1 = -nR \ln \frac{p_\mathrm{f}}{p_\mathrm{i}} = -(1.00\ \mathrm{mol})\left(8.314\ \frac{\mathrm{J}}{\mathrm{mol{\cdot}K}}\right) \ln \frac{15.0\ \mathrm{atm}}{1.50\ \mathrm{atm}}$$

$$\Delta S_1 = -19.1\ \frac{\mathrm{J}}{\mathrm{K}}$$

For the second step, the isobaric step, we use equation 3.18:

$$\Delta S_2 = C \ln \frac{T_\mathrm{f}}{T_\mathrm{i}} = (1.00\ \mathrm{mol})\left(20.78\ \frac{\mathrm{J}}{\mathrm{mol{\cdot}K}}\right) \ln \frac{100.0\ \mathrm{K}}{298.0\ \mathrm{K}}$$

$$\Delta S_2 = -22.7\ \frac{\mathrm{J}}{\mathrm{K}}$$

The overall change in entropy is the sum of the two, just as the overall process is the combination of the two steps. We get $\Delta S = -19.1 + (-22.7)\ \mathrm{J/K} = -41.8\ \mathrm{J/K}$.

Consider the system illustrated in Figure 3.4a. A container is divided into two systems having volumes V_1 and V_2, but both systems have the same pressure p and the same absolute temperature T. The number of moles of different ideal gases in side 1 and side 2 are n_1 and n_2, respectively. A barrier separates the two sides. We will assume that the systems are isolated from the surroundings so that q is zero for the following process (that is, it is adiabatic).

At some point, the barrier is removed while maintaining the overall pressure and temperature. Since the process is adiabatic, $q = 0$. Since the temperature is constant, $\Delta U = 0$ also. Therefore, $w = 0$. However, the two gases mix so that our final system looks like Figure 3.4b: two mixed gases occupying the same volume. (This agrees with our conventional wisdom regarding the behavior of gases: they expand to fill their container.) Since there is no energy change to cause the mixing, then it must be entropy that is causing the process.

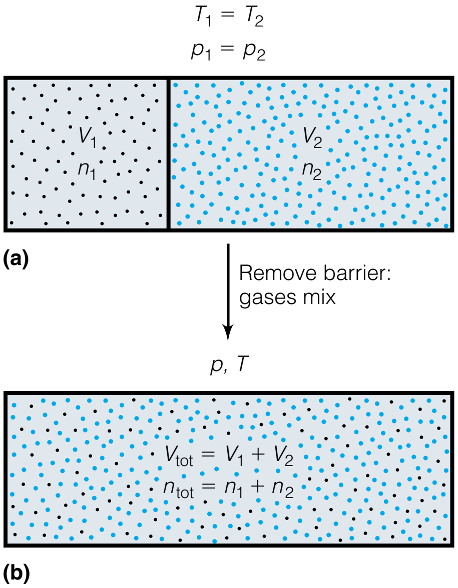

Figure 3.4 The adiabatic mixing of two gases. (a) On the left side is gas 1 with a certain volume and amount, and on the right side is gas 2 with its own volume and amount. (b) After mixing, both gases occupy the complete volume. Since there is no energy change to cause the gases to mix, the mixing must have been caused by entropy effects.

Entropy is a state function, so the change in entropy is path-independent. Consider that the mixing process can be broken down into two individual steps, as illustrated in Figure 3.5. One process is the expansion of gas 1 from V_1 to V_tot, and the other process is the expansion of gas 2 from V_2 to V_tot. Using ΔS_1 and ΔS_2 to represent the changes in entropies for the steps, we have

$$\Delta S_1 = n_1 R \ln \frac{V_\mathrm{tot}}{V_1}$$

$$\Delta S_2 = n_2 R \ln \frac{V_\mathrm{tot}}{V_2}$$

Since V_tot is greater than V_1 or V_2 (because both gases are expanding), the logarithms of the volume fractions will always be positive. (Logarithms of numbers greater than 1 are positive.) The ideal gas law constant is always positive, and the number of moles of each gas is also positive. Therefore, the individual entropy changes will be positive overall, and the combination of the two components to get ΔS for the mixing process

$$\Delta S = \Delta S_1 + \Delta S_2 \tag{3.21}$$

will always be positive. Therefore, by the second law of thermodynamics, the mixing of two (or more) gases is always a spontaneous process if it occurs in an isolated system.

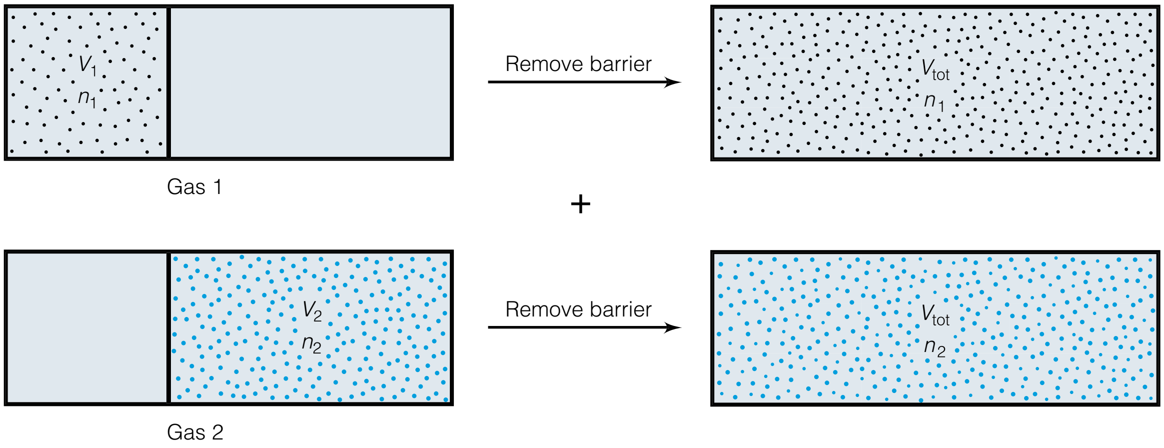

Figure 3.5 The mixing of two gases can be separated into two individual processes, where gas 1 expands into the right side and gas 2 expands into the left side.

There is another way of generalizing equation 3.21. If two or more gas samples have the same pressure and temperature, then their volumes are directly proportional to the number of moles of gas present. The *mole fraction of gas i*, x_i, is defined as the ratio of the number of moles of gas i, n_i, and the total number of moles of gas, n_{tot}:

$$x_i = \frac{n_i}{n_{tot}} \tag{3.22}$$

It can be shown that

$$\frac{V_i}{V_{tot}} = \frac{n_i}{n_{tot}} = x_i$$

so that the expression for the overall entropy can be expressed as

$$\Delta S = (-n_1 R \ln x_1) + (-n_2 R \ln x_2)$$

The negative signs are introduced because in order to substitute the mole fraction into the expression, we have to take the reciprocal of the volume fraction. For any number of gases being mixed:

$$\Delta_{mix} S = -R \cdot \sum_{i=1}^{\text{no. of gases}} n_i \ln x_i \tag{3.23}$$

where $\Delta_{mix} S$ is referred to as the *entropy of mixing*. Because x_i is always less than 1 (for two or more components), its logarithm is always negative. The negative sign as part of equation 3.23 means that the entropy of mixing is always a sum of positive terms and the overall $\Delta_{mix} S$ is always *positive*.

Example 3.4

Calculate the entropy of mixing 10.0 L of N_2 with 3.50 L of N_2O at 300.0 K and 0.550 atm. Assume that the volumes are additive; that is, V_{tot} = 13.5 L.

Solution

We need to determine the number of moles of each component in the resulting mixture. Given all of the conditions, we can use the ideal gas law to calculate them:

$$n_{N_2} = \frac{pV}{RT} = \frac{(0.550\ \text{atm})(10.0\ \text{L})}{(0.08205\ \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(300.0\ \text{K})} = 0.223\ \text{mol}\ N_2$$

$$n_{N_2O} = \frac{pV}{RT} = \frac{(0.550\ \text{atm})(3.50\ \text{L})}{(0.08205\ \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(300.0\ \text{K})} = 0.078\ \text{mol}\ N_2O$$

Since the total number of moles is 0.223 mol + 0.078 mol = 0.301 mol, we can now calculate the mole fractions of each component:

$$x_{N_2} = \frac{0.223\ \text{mol}}{0.301\ \text{mol}} = 0.741$$

$$x_{N_2O} = \frac{0.078\ \text{mol}}{0.301\ \text{mol}} = 0.259$$

(Note that the sum of the mole fractions is 1.000, as required.) We can use equation 3.23 to determine $\Delta_{\text{mix}}S$:

$$\Delta_{\text{mix}}S = -8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}}(0.223\ \text{mol} \cdot \ln 0.741 + 0.078\ \text{mol} \cdot \ln 0.259)$$

The mol units cancel and we evaluate to find

$$\Delta_{\text{mix}}S = +1.43\ \frac{\text{J}}{\text{K}}$$

Notice that this problem uses two different values for R, the ideal gas law constant. In each case, the choice was dictated by the units that were necessary to solve that particular part of the problem.

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Figure 3.6 Ludwig Edward Boltzmann (1844–1906), Austrian physicist. Boltzmann used the relatively young idea of atoms to develop a statistical mathematical description of matter, which eventually introduced the concept of order as a measure of entropy. Although his work is of profound importance in thermodynamics, the wrangling over ideas and critiques at that crucial period in the history of science is thought to have been a contributing factor in his suicide.

3.6 Order and the Third Law of Thermodynamics

The preceding discussion of the entropy of mixing brings us to a useful general idea regarding entropy, that of *order*. Having two pure gases on either side of a barrier is a nice, neat, relatively ordered arrangement. Mixing the two of them, a process that occurs spontaneously, is a more random, less ordered arrangement. So this system proceeds spontaneously from a more ordered system to a less ordered system.

In the mid- to late-1800s, the Austrian physicist Ludwig Edward Boltzmann (Figure 3.6) began applying the mathematics of statistics to the behavior of matter, especially gases. In doing so, Boltzmann was able to determine a different definition for entropy. Consider a system of gas molecules that all have the same chemical identity. The system can be broken up into smaller microsystems whose individual states contribute statistically to the overall state of the system. For any particular number of microsystems, there are a certain number of ways of distributing the gas molecules into the microsystems. If the most probable distribution has Ω different ways of arranging the particles,*

---

*For example, say you have a simple system consisting of two balls and four shoe boxes. There are 10 possible arrangements for putting the balls in the boxes: four arrangements with both balls in a single box (the other three are empty), and six arrangements with one ball in each of two boxes (the other two are empty). The most probable arrangement is one ball in each of two boxes, and there are six different ways of getting that arrangement. Therefore, Ω equals 6 in this case. Chapter 17 gives more details on this and other concepts relating to Boltzmann's interpretation of entropy.

Boltzmann found that the *absolute entropy* S of the system is proportional to the natural logarithm of the number of possible combinations:

$$S \propto \ln \Omega$$

To make a proportionality an equality, a proportionality constant is necessary:

$$S = k \ln \Omega \tag{3.24}$$

where k is known as *Boltzmann's constant.*

There are several important ramifications of equation 3.24. First, it introduces the concept that an *absolute* entropy can be determined. Entropy thus stands alone among state functions as the only one whose absolute values can be determined. Therefore, in large thermodynamic tables of ΔU and ΔH values, parallel entries for entropy are for S, not ΔS. It also implies that the entropies found in tables are not zero for elements under standard conditions, because we are now tabulating *absolute* entropies, not entropies for formation reactions. We can determine *changes* in entropies, ΔS's, for processes; up to now we have dealt exclusively with changes in entropy. But Boltzmann's equation 3.24 means that we can determine absolute values for entropy.

Second, equation 3.24 brings up an intriguing notion. Consider a system where all species (atoms or molecules) of the component are in the same state. One way of illustrating this is to assume that it is in the form of a perfect crystal, implying perfect order. If this was the case, then Ω (the number of possible combinations of conditions that would have this arrangement) would be 1, the logarithm of Ω would be zero, and thus S would be zero. It seems unlikely that such a circumstance might exist under normal conditions.

However, science has the ability to dictate the conditions of systems under study. In the late 1800s and early 1900s the properties of matter at extremely low temperatures were being investigated. As the thermodynamics of materials were measured at temperatures approaching absolute zero, the total entropy of cold, crystalline materials—which could be measured experimentally using expressions like equation 3.18—began approaching zero. Since entropy is an obvious function of T for all substances, the following mathematical statement became obvious:

$$\lim_{T \to 0\text{K}} S(T) = 0 \quad \text{for a perfectly crystalline material} \tag{3.25}$$

This is the third law of thermodynamics, which can be stated verbally as follows:

> The third law of thermodynamics: Absolute entropy approaches zero as the absolute temperature approaches zero.

Thus, this statement provides entropy with an absolute minimum value of zero and establishes the ability to determine absolute entropies. Equation 3.24, defining a statistical origin of entropy, is such a fundamental idea in science that it is carved on Ludwig Boltzmann's tombstone in Vienna. (See Figure 3.7.)

Boltzmann's constant is, interestingly enough, related to the ideal gas law constant R. It can be shown that

$$R = N_A \cdot \text{k} \tag{3.26}$$

where N_A is Avogadro's number ($= 6.022 \times 10^{23}$). The constant k therefore has a value of 1.381×10^{-23} J/K. Its relative magnitude implies that there are an enormous number of possible combinations of states that atoms and molecules of macroscopic samples can adopt, as seen in the following example.

Courtesy of Frantisek Zboray, Vienna

Figure 3.7 Above the bust of Boltzmann, you might be able to make out the equation $S = k \ln \Omega$.

Example 3.5

The absolute entropy of Fe (s) at 25.0°C and standard pressure is 27.28 J/mol·K. Approximately how many possible combinations of states are available to a collection of 25 Fe atoms under those conditions? Does the answer suggest why the system is being limited to only 25 atoms?

Solution

Using Boltzmann's equation for entropy:

$$\left(\frac{25 \text{ atoms}}{6.022 \times 10^{23} \text{ atoms/mol}}\right) 27.28 \frac{\text{J}}{\text{mol}\cdot\text{K}} = \left(1.381 \times 10^{-23} \frac{\text{J}}{\text{K}}\right)(\ln \Omega)$$

Solving, we find

$$\ln \Omega = 82.01$$

$$\Omega = 4.12 \times 10^{35}$$

which is an incredible number of possible states for just 25 atoms! However, the sample is at a relatively high temperature, 298 K. We will see in later chapters how this implies a huge kinetic energy for such a small system.

Example 3.6

Rationalize the following order of absolute molar entropies at 298 K:

$$\overline{S}[\text{N}_2\text{O}_5\ (\text{s})] < \overline{S}[\text{NO}\ (\text{g})] < \overline{S}[\text{N}_2\text{O}_4\ (\text{g})]$$

Solution

If we apply the idea that entropy is related to the number of states accessible to the system, then we can argue immediately that a system of a solid phase should have fewer states accessible to it. Therefore, it should have the lowest entropy of the three materials given. Of the remaining two, both materials are gases. However, one gas is composed of diatomic molecules while the other is composed of molecules with six atoms. It can be argued that the diatomic molecule will have fewer states available to it than will a hexatomic molecule, so $\overline{S}[\text{NO (g)}]$ will probably be less than $\overline{S}[\text{N}_2\text{O}_4\text{ (g)}]$. You can verify this order by consulting a table of experimental entropies for compounds (like the one in Appendix 2).

3.7 Entropies of Chemical Reactions

We have already used the idea of combining the changes in entropy of various individual steps to determine the change in entropy of the combination of those steps. We can use such ideas to determine the changes in entropy that occur with chemical reactions. The situation is only slightly different, because we can determine the *absolute* entropies of the chemical reactants and products. Figure 3.8 illustrates the concept for a process where ΔS is negative, that is, entropy is going down. As such, we do not need to rely on formation reactions but can state that the change in entropy of a chemical reaction equals the combined entropies of the products minus the combined entropies of the reactants. Thus,

$$\Delta_{\text{rxn}} S = \sum_{\text{products}} S - \sum_{\text{reactants}} S \tag{3.27}$$

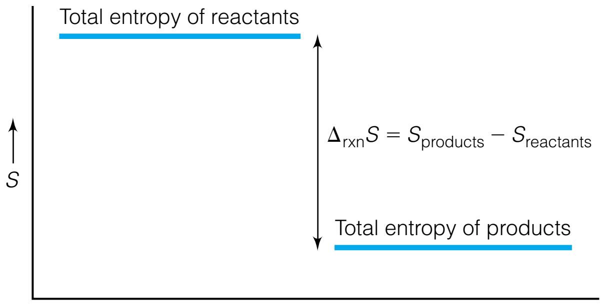


Figure 3.8 Entropy can change for a reaction, just like enthalpy can change. In this case, the entropy of the products is less than that of the reactants, so the $\Delta_{rxn}S$ is negative.

where the S(products) and S(reactants) represent the absolute entropy of the chemical species involved in the process. If standard conditions apply, every entropy term can have a degree symbol ° appended:

$$\Delta_{rxn}S^\circ = \sum_{\text{products}} S^\circ - \sum_{\text{reactants}} S^\circ$$

Changes in entropy for chemical processes can be considered using the above Hess's-law type of approach.

Example 3.7

Using the table in Appendix 2, determine the change in entropy for the following chemical reaction occurring at standard pressure and the stated temperature:

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (\ell)$$

Solution

From the table, $S^\circ[H_2\ (g)] = 130.7$ J/mol·K, $S^\circ[O_2\ (g)] = 205.1$ J/mol·K, and $S^\circ[H_2O,\ (\ell)] = 69.91$ J/mol·K. Keeping in mind that the balanced chemical reaction gives molar ratios of reactants and products, equation 3.27 yields

$$\Delta_{rxn}S^\circ = \underbrace{[2 \cdot 69.91]}_{\sum_{\text{products}} S^\circ} - \underbrace{[2 \cdot 130.7 + 205.1]}_{\sum_{\text{reactants}} S^\circ}\ \text{J/K}$$

where the entropies of the products and reactants are labeled. The mol units cancel because we are including the stoichiometry explicitly: 2 mol H_2O as products, and 2 mol H_2 and 1 mol O_2 as reactants. Evaluating:

$$\Delta_{rxn}S^\circ = -326.7\ \text{J/K}$$

That is, during the course of the reaction, the entropy is decreasing by 326.7 J/K. Does this make sense, in terms of entropy as a measure of the number of accessible states? The balanced chemical reaction is showing 3 moles of gas reacting to make 2 moles of liquid. It can be argued that a condensed phase will have fewer accessible states than a gas will, and the actual number of molecules is decreasing. Therefore, a decrease in entropy is understandable.

As with ΔH, there are many times when ΔS needs to be determined for a process that occurs at different temperatures and pressures. Equation 3.18, or its form in terms of number of moles of substance, gives us a way to determine ΔS for a process where temperature is changing:

$$\Delta S = n\overline{C} \ln \frac{T_f}{T_i} \qquad \mathbf{(3.18)}$$

Just like evaluating ΔH at different temperatures, we have a scheme for determining ΔS at different temperatures:

1. Use equation 3.18 to evaluate the change in entropy for the reactants as they go from their initial temperature to a reference temperature, usually 298 K.
2. Use the entropies from the tabulated data to determine the entropy change of the reaction at the reference temperature.
3. Use equation 3.18 again to evaluate the change in entropy for the products as they go from the reference temperature to the original temperature.

The entropy change at the specified temperature is the sum of these three entropy changes. We are taking advantage of the fact that entropy is a state function: the change is dictated by the change in the conditions, not how the system got there. Therefore, our three-step process, which is equivalent to performing the change in a single step at the stated temperature, has the same entropy change as the one-step process. (The assumption is that the heat capacity, C, does not vary with temperature. It does, but for small ΔT values this assumption is a very good approximation.)

Gas-phase processes occurring under nonstandard pressures are also easily calculated in terms of either the changing pressures or volumes of the system. The following two equations were derived earlier in this chapter.

$$\Delta S = nR \ln \frac{V_f}{V_i} \qquad \mathbf{(3.19)}$$

$$\Delta S = -nR \ln \frac{p_f}{p_i} \qquad \mathbf{(3.20)}$$

These equations can also be used in a stepwise fashion as described above for nonstandard temperature.

Example 3.8

What is the entropy change of the reaction

$$2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(\ell)$$

at 99°C and standard pressure? Treat the heat capacities of H_2, O_2, and H_2O as constant at 28.8, 29.4, and 75.3 J/mol·K, respectively. Assume molar quantities based on the balanced chemical reaction and ideal gas behavior.

Solution

1. The first step is to determine the change in entropy as the reactants, 2 moles of H_2 and 1 mole of O_2, change temperature from 99°C to 25°C (which is 372 K to 298 K). This is labeled ΔS_1. It is, according to equation 3.18:

$$\Delta S_1 = (2\text{ mol})\left(28.8\,\frac{\text{J}}{\text{mol·K}}\right)\ln\frac{298\text{ K}}{372\text{ K}} + (1\text{ mol})\left(29.4\,\frac{\text{J}}{\text{mol·K}}\right)\ln\frac{298\text{ K}}{372\text{ K}}$$

$$\Delta S_1 = -19.3\,\frac{\text{J}}{\text{K}}$$

2. The second step is to evaluate the change in entropy at the reference temperature, 298 K. We will label this ΔS_2. This was, in fact, calculated in Example 3.7. It is

$$\Delta S_2 = -326.7\ \frac{\text{J}}{\text{K}}$$

3. The third step is to evaluate the change in entropy as we bring the products from the reference temperature to the specified reaction temperature (that is, from 298 K to 372 K). This entropy change is labeled ΔS_3. According to equation 3.18:

$$\Delta S_3 = (2\ \text{mol})\left(75.3\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\ln\frac{372\ \text{K}}{298\ \text{K}}$$

$$\Delta S_3 = 33.4\ \frac{\text{J}}{\text{K}}$$

The overall entropy change is the sum of the three individual entropy values:

$$\Delta_{\text{rxn}}S = -19.3 - 326.7 + 33.4\ \frac{\text{J}}{\text{K}}$$

$$\Delta_{\text{rxn}}S = -312.6\ \frac{\text{J}}{\text{K}}$$

Although the change in entropy is similar to that at 25°C, it is slightly different. This is an example of a relatively minor change in conditions. If the temperatures were hundreds of degrees different from the reference temperature, large changes in ΔS would be seen. If this were the case, temperature-dependent functions would have to be used for the heat capacities, since their being constant is also an approximation.

Example 3.9

What is the entropy change of the reaction

$$2\text{H}_2\ (\text{g}) + \text{O}_2\ (\text{g}) \longrightarrow 2\ \text{H}_2\text{O}\ (\ell)$$

at 25°C and 300 atm? Assume molar quantities based on the balanced chemical reaction. Assume also that a pressure change does not affect the entropy of the liquid water product (that is, $\Delta S_3 = 0$).

Solution

This example is similar to Example 3.8, except that the pressure is nonstandard. Since ΔS_3 is approximated as zero, we need only evaluate the ΔS's of the first two steps:

1. The change in entropy as the pressure of the reactants goes from 300 atm to the standard pressure of 1 atm is

$$\Delta S_1 =$$
$$-(2\ \text{mol})\left(8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\ln\frac{1\ \text{atm}}{300\ \text{atm}} - (1\ \text{mol})\left(8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\ln\frac{1\ \text{atm}}{300\ \text{atm}}$$

where the first term is for the hydrogen and the second term is for the oxygen. Solving:

$$\Delta S_1 = +142.3\ \frac{\text{J}}{\text{K}}$$

2. The second part is for the reaction at standard conditions. Again, that has already been evaluated in Example 3.7, and is

$$\Delta S_2 = -326.7 \frac{\text{J}}{\text{K}}$$

3. The third part is assumed to be zero:

$$\Delta S_3 = 0 \frac{\text{J}}{\text{K}}$$

The overall $\Delta_{\text{rxn}}S$ is the combination of the three:

$$\Delta_{\text{rxn}}S = +142.3 - 326.7 + 0 \frac{\text{J}}{\text{K}}$$

$$\Delta_{\text{rxn}}S = -184.4 \frac{\text{J}}{\text{K}}$$

The effects of entropy are seen at a biological level, as well. The joining of two single strands of RNA or DNA is accompanied by a small decrease in enthalpy (about 40 kJ/mol per base pair), as expected for hydrogen-bonding interactions. There is also a nontrivial entropy change, about −90 J/mol·K per base pair. Compare this value to the entropy of combustion in Example 3.9.

3.8 Summary

In this chapter, we have introduced a new state function: entropy. It will have a unique impact on our study of thermodynamics. It is not an energy, like internal energy or enthalpy: it is a different kind of state function, a different quantity. One way to think of it, as introduced by Boltzmann, is as a measure of the number of states available to a system.

The definition of entropy ultimately brings us to an idea that we call the second law of thermodynamics: that for an isolated system, any spontaneous change occurs with a concurrent increase in the entropy of the system. The mathematical definition of entropy, in terms of the change in heat for a reversible process, allows us to derive many mathematical expressions we can use to calculate the entropy change for a physical or chemical process. The concept of order brings us to what we call the third law of thermodynamics: that the absolute entropy of a perfect crystal at absolute zero is exactly zero. We can therefore speak of absolute entropies of materials at temperatures other than 0 K. Entropy becomes—and will remain—the only thermodynamics state function for a system that we can know absolutely. (Contrast this with state *variables* like p, V, T, and n, whose values we can also know absolutely.)

We began this chapter with the question of spontaneity. Will a process occur by itself? If the system is isolated, we have an answer: it will if the entropy increases. But most processes are not truly isolated. Many systems allow for energy to move in and out (that is, are closed, not isolated, systems). In order to have a truly useful spontaneity test, we have to consider changes in energy as well as changes in entropy. We will introduce such considerations in the next chapter.

3.2 Limits of the First Law

3.1. Decide whether the following processes will be spontaneous, and why. The "why" can be general, not specific. **(a)** Ice melting at +5°C **(b)** Ice melting at −5°C **(c)** KBr (s) dissolving in water **(d)** An unplugged refrigerator getting cold **(e)** A leaf falling from a tree to the ground **(f)** The reaction $Li\ (s) + \frac{1}{2}F_2\ (g) \rightarrow LiF\ (s)$ **(g)** The reaction $H_2O\ (\ell) \rightarrow H_2\ (g) + \frac{1}{2}O_2\ (g)$

3.2. Try to find one additional example of a spontaneous process that is in fact endothermic; that is, it occurs with an absorption of heat.

3.3 Carnot Cycle and Efficiency

3.3. Consider the following quantities for a Carnot-type cycle: Step 1: $q = +850$ J, $w = -334$ J. Step 2: $q = 0$, $w = -115$ J. Step 3: $q = -623$ J, $w = +72$ J. Step 4: $q = 0$, $w = +150$ J. Calculate the efficiency of the cycle.

3.4. Consider the following quantities for a four-step cycle: Step 1: $q = +445$ J, $w = -220$ J. Step 2: $q = 0$, $w = -99$ J. Step 3: $q = -660$ J, $w = +75$ J. Step 4: $q = 0$, $w = +109$ J. Under what additional conditions for each step will this be a Carnot-type cycle? What is the efficiency of this process?

3.5. At what temperature is the low-temperature reservoir of a process that has an efficiency of 0.440 (44.0%) and a high-temperature reservoir at 150°C?

3.6. What is the efficiency of an engine whose T_{high} is 100°C and whose T_{low} is 0°C?

3.7. Superheated steam is steam with a temperature greater than 100°C. Explain the advantages of using superheated steam to run a steam engine.

3.8. The Carnot cycle is defined as having a certain specific first step, the isothermal expansion of a gas. Can a Carnot cycle start at step 2, the adiabatic expansion? Why or why not? (*Hint:* See Figure 3.2.)

3.9. How does a perpetual motion machine violate the first law of thermodynamics?

3.10. A refrigerator is the reverse of an engine: work is performed to remove heat from a system, making it colder. The efficiency of a refrigerator (often termed the "coefficient of performance") is defined as $q_3/w_{\text{cycle}} = T_{\text{low}}/(T_{\text{high}} - T_{\text{low}})$. Use this definition to determine the efficiency needed to halve the absolute temperature. What does your answer imply about attempts to reach absolute zero?

3.11. Efficiency is given by equations 3.5, 3.6, and 3.10. Although we deal mostly with ideal gases in the development of thermodynamics, experimentally we are confined to real gases. Which of the definitions of e are strictly applicable to processes involving real gases as well as ideal gases?

3.4 & 3.5 Entropy and the Second Law

3.12. What is the entropy change for the melting of 3.87 moles of bismuth at its melting point of 271.3°C? The heat of fusion of solid Bi is 10.48 kJ/mol. (Bismuth is one of the few materials, including water, that is less dense in solid form than in liquid; therefore, solid Bi floats in liquid Bi, like ice floats in water.)

3.13. Explain why the statement "No process is 100% efficient" is not the best statement of the second law of thermodynamics.

3.14. What is the change in entropy of 1.00 mole of water as it is heated reversibly from 0°C to 100°C? Assume that the heat capacity is constant at 4.18 J/g·K.

3.15. The heat capacity of solid gold, Au, is given by the expression

$$C = 25.69 - 7.32 \cdot 10^{-4}T + 4.58 \cdot 10^{-6}\ T^2\ \frac{\text{J}}{\text{mol·K}}$$

Evaluate the change in entropy for 2.50 moles of Au if the temperature changes reversibly from 22.0°C to 1000°C.

3.16. One mole of He warms up irreversibly at constant volume from 45°C to 55°C. Is the change in entropy less than, equal to, or greater than 0.386 J/K? Explain your answer.

3.17. A normal breath has a volume of about 1 L. The pressure exerted by the lungs to draw air in is about 758 torr. If the surrounding air is at exactly 1 atm (= 760 torr), calculate the change in entropy exerted on a breath of air due to its being inhaled into the lungs. (*Hint:* you will have to determine the number of moles of gas involved.)

3.18. A sample of (ideal) gas from a compressed gas cylinder goes from 230 atm to 1 atm, with a concurrent change of volume wherein 1 cm^3 expands to 230 cm^3 in volume. Assume that the temperature remains (or becomes) the same for the initial and final states. Calculate the change in entropy for 1 mole of the gas undergoing this process. Does your answer make sense? Why or why not?

3.19. If a 1-mole sample of a real gas from a compressed gas cylinder goes from 230 atm to 1 atm and from a volume of 1 cm^3 to 195 cm^3, what is the entropy change for the expansion if it is assumed to be isothermal? Does this agree with the second law of thermodynamics?

3.20. Derive equation 3.20. How does the minus sign show up?

3.21. In Example 3.3, a heat capacity of 20.78 J/mol·K was used, which is 5/2 R. Is this value of the heat capacity justified? Why?

3.22. What is the entropy of mixing to make 1 mole of air from its constituent elements? Air can be assumed to be 79% N_2, 20% O_2, and 1% Ar. Assume ideal gas behavior.

3.23. 4.00 L of Ar and 2.50 L of He, each at 298 K and 1.50 atm, were mixed isothermically and isobarically. The mixture was then expanded to a final volume of 20.0 L at 298 K. Write chemical reactions for each step, and determine the change in entropy for the complete process.

3.24. Dentists might use a mixture of 40% N_2O and 60% O_2 as an initial anesthetic of nitrous oxide (although the exact proportions may vary). Determine the entropy of mixing for 1 mole of such a mixture. Assume ideal gas conditions.

3.25. A 5.33-g piece of Cu metal is heated to 99.7°C in boiling water, then dropped into a calorimeter containing 99.53 g of H_2O at 22.6°C. The calorimeter is sealed to the outside environment, and temperature equalizes. $C_p[\text{Cu (s)}] = 0.385\ \text{J/g·K}$, $C_p[H_2O] = 4.18\ \text{J/g·K}$. **(a)** Discuss the process that occurs inside the calorimeter in terms of the zeroth and first laws of thermodynamics. **(b)** What is the final temperature inside the system? **(c)** What is the entropy change of the Cu (s)? **(d)** What is the entropy change of the H_2O (ℓ)? **(e)** What is the total entropy change in the system? **(f)** Discuss the process that occurs inside the calorimeter in terms of the second law of thermodynamics. Do you expect it to be spontaneous?

3.26. In the last exercise, neither Cu nor H_2O is an ideal gas. Comment on the expected reliability of your answers for ΔS for parts c, d, and e. (*Hint:* consider the derivation of the equation you used to calculate ΔS.)

3.27. The first law of thermodynamics is sometimes stated "You can't win" and the second law is stated similarly as "You can't even break even." Explain how these two statements can be considered apt (though incomplete) viewpoints for the first and second laws of thermodynamics.

3.28. Trouton's rule states that the entropy of boiling at the normal point is 85 J/mol·K. **(a)** Does the data from Example 3.2 support Trouton's rule? **(b)** H_2O has a heat of vaporization of 40.7 kJ/mol. Does the $\Delta_{\text{vap}}S$ for H_2O at its normal boiling point support Trouton's rule? Can you explain any deviation? **(c)** Predict the boiling point of cyclohexane, C_6H_{12}, if its $\Delta_{\text{vap}}H$ is 30.1 kJ/mol. Compare your answer to the measured normal boiling point of 80.7°C.

3.6 Order and the Third Law of Thermodynamics

3.29. Argue from Boltzmann's definition for entropy that S can never have a negative value. (*Hint:* see equation 3.24.)

3.30. Calculate the value of Boltzmann's constant in units of **(a)** L·atm/K and **(b)** (cm^3·mmHg)/K.

3.31. Which system has the higher entropy? **(a)** A clean kitchen or a dirty kitchen? **(b)** A blackboard with writing on it or a completely erased blackboard? **(c)** 1 g of ice at 0°C or 10 g of ice at 0°C? **(d)** 1 g of ice at 0 K or 10 g of ice at 0 K? **(e)** 10 g of ethyl alcohol, C_2H_5OH, at 22°C (roughly room temperature) or 10 g of ethyl alcohol at 2°C (the approximate temperature of a cold drink)?

3.32. Which system has the higher entropy? **(a)** 1 g of solid Au at 1064 K or 1 g of liquid Au at 1064 K? **(b)** 1 mole of CO at STP or 1 mole of CO_2 at STP? **(c)** 1 mole of Ar at a pressure of 1 atm or 1 mole of Ar at a pressure of 0.01 atm?

3.33. The element helium is thought to remain a liquid at absolute zero. (Solid helium can be made only by exerting a pressure of about 26 atm on a liquid sample.) Is the entropy of liquid helium at absolute zero exactly zero? Why or why not?

3.34. Order the following substances in order of increasing entropy: NaCl (solid), C (graphite), C (diamond), $BaSO_4$ (solid), Si (crystal), Fe (solid).

3.7 Entropies of Chemical Reactions

3.35. Why isn't the entropy of elements in their standard pressure at normal (that is, room) temperatures equal to zero?

3.36. Determine the entropy of formation, $\Delta_f S$, of the following compounds. Assume 25°C. **(a)** H_2O (ℓ) **(b)** H_2O (g) **(c)** $Fe_2(SO_4)_3$ **(d)** Al_2O_3 **(e)** C (diamond)

3.37. The thermite reaction has solid aluminum powder reacting with iron(III) oxide to make aluminum oxide and iron. The reaction is so exothermic that the iron product is usually molten initially. Write the balanced chemical reaction for the thermite reaction and determine the $\Delta_{\text{rxn}}S$ for the process. Assume standard conditions.

3.38. In place of iron(III) oxide in the thermite reaction in the previous problem, chromium(III) oxide can be used in its place, generating chromium metal and aluminum oxide as products. Calculate $\Delta_{\text{rxn}}H$ and $\Delta_{\text{rxn}}S$ for this thermite-type reaction. Assume standard conditions.

3.39. Determine the differences in the $\Delta_{\text{rxn}}S$ under standard conditions for the two following reactions:

$$H_2\ (g) + \tfrac{1}{2}O_2\ (g) \longrightarrow H_2O\ (\ell)$$

$$H_2\ (g) + \tfrac{1}{2}O_2\ (g) \longrightarrow H_2O\ (g)$$

and justify the difference.

3.40. What is the change in entropy when 2.22 mol of water is heated from 25.0°C to 100°C? Assume that the heat capacity is constant at 4.18 J/g·K.

3.41. Estimate the entropy change of an 800-lb engine (1 lb = 2.2 kg) that goes from normal environmental temperature, about 20°C, to an average operational temperature of 650°C. The heat capacity of iron (the major component of most engines) is 0.45 J/g·K.

3.42. Calculate the molar entropy change of the gas that accompanies the bursting of a balloon if the initial pressure is 2.55 atm and the external pressure is 0.97 atm.

3.43. A normal breath is about 1 L in volume. Assume you take a breath at sea level, where the pressure is 760 mmHg. Then you instantly (this is a thought experiment, after all) go to Los Alamos, New Mexico, located in the mountains where the normal atmospheric pressure is 590 mmHg, and you exhale. Assuming ideal gas behavior, what's the change in entropy of the air? Assume a temperature of 37°C.

Symbolic Math Exercises

3.44. Set up expressions to calculate the work and heat for the four steps of a Carnot cycle. Define initial conditions for pressure and volume of a given amount (say, 1 mole) of an ideal gas, and calculate w and q for each step in the cycle and the total work and heat of the cycle. Show that $\Delta S = 0$ for the cycle if it is done reversibly. You may have to specify other variables.

3.45. Numerically determine ΔS for the isobaric change in temperature of 4.55 g of gallium metal as it is heated from 298 K to 600 K if its molar heat capacity is given by the expression $C_p = 27.49 - 2.226 \times 10^{-3}T + 1.361 \times 10^5/T^2$. Assume standard units on the expression for heat capacity.

3.46. Plots of C_p/T versus T are used to determine the entropy of a material, as the entropy value would be the area under the curve. For sodium sulfate, Na_2SO_4, the following data are available:

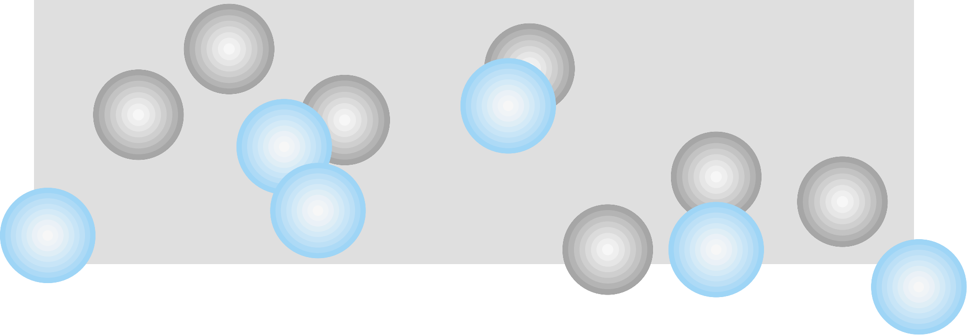
T (K)	C_p (cal/K)
13.74	0.171
16.25	0.286
20.43	0.626
27.73	1.615
41.11	4.346
52.72	7.032
68.15	10.48
82.96	13.28
95.71	15.33

Source: G. N. Lewis and M. Randall, *Thermodynamics,* rev. K. Pitzer and L. Brewer, McGraw-Hill, New York, 1961

Extrapolate to 0 K using a function $f(T) = kT^3$, where k is some constant. Using your plot, numerically evaluate the experimental entropy of Na_2SO_4 at 90 K.

4

Free Energy and Chemical Potential



WE STARTED THE LAST CHAPTER with the question, "Will a process occur spontaneously?" Although we introduced the concept of entropy as a basis for answering that question, we did not completely answer it. The second law of thermodynamics is strictly applicable to an *isolated* system, in which no other discernible change in a thermodynamic state function occurs. For such systems, spontaneous processes do occur if they are accompanied by an increase in the entropy of a system. But most systems are not isolated (in fact, the only truly isolated system is the entire universe), and most changes involve more than a change in entropy. Many processes occur with a simultaneous change in energy. You may recall the idea that most spontaneous changes are exothermic. Many endothermic changes are also spontaneous. A proper thermodynamic definition of a spontaneous process takes *both* energy and entropy changes into account.

4.1 Synopsis

We will begin the chapter by discussing the limitations of entropy. We will then define the Gibbs free energy and the Helmholtz energy. What we will ultimately show is that for most chemical processes, the Gibbs free energy provides a strict test for the spontaneity or nonspontaneity of that process.

The Gibbs and Helmholtz energies, both named after prominent thermodynamicists, are the last energies that will be defined. Their definitions, coupled with the appropriate use of partial derivation, allow us to derive a rich set of mathematical relationships. Some of these mathematical relationships let the full force of thermodynamics be applied to many phenomena, like chemical reactions and chemical equilibria and—importantly—predictions of chemical occurrences. These relationships are used by some as proof that physical chemistry is complicated. Perhaps they are better seen as proof that physical chemistry is widely applicable to chemistry as a whole.

4.2 Spontaneity Conditions

The derivation of the equation

$$\Delta S > 0 \tag{4.1}$$

as a measure of spontaneity is limited in application, since it applies to isolated systems on which no work is done and which are adiabatic, so that both w and q are zero. We recognize, however, that many processes occur with $w \neq 0$ and/or $q \neq 0$. What we really want is a way to determine spontaneity for experimental conditions that are common in real life. These conditions are *constant pressure* (because many processes occur when exposed to atmospheric pressure, which is usually constant over the course of the experiment) and *constant temperature* (which is the easiest state variable to control).

Internal energy and enthalpy can also be used to determine spontaneity under appropriate conditions. Consider equation 4.1. Since $w = 0$ and $q = 0$, the process is occurring at constant U, and we can label the infinitesimal change in entropy dS with these constant state variables:

$$(dS)_{U,V} > 0 \tag{4.2}$$

where the subscripts U, V indicate what variables are held constant. Let us determine different spontaneity conditions for different conditions. The Clausius theorem for a spontaneous change is:

$$\frac{dq_{\text{rev}}}{T} \leq dS$$

We can rewrite this as

$$\frac{dq_{\text{rev}}}{T} - dS \leq 0$$

and since we know that $dU = dq_{\text{rev}} - p_{\text{ext}}\,dV$, or $dq_{\text{rev}} = dU + p_{\text{ext}}\,dV$,

$$\frac{dU + p_{\text{rev}}\,dV}{T} - dS \leq 0$$

The "equal to" part of the sign applies if the process is reversible. Multiplying through by T, we get for a spontaneous change,

$$dU + p\,dV - T\,dS \leq 0$$

If the process occurs under conditions of constant volume and constant entropy, that is, dV and dS are zero, this equation becomes

$$(dU)_{V,S} \leq 0 \tag{4.3}$$

as a spontaneity condition. Because this condition depends on volume and entropy staying constant, V and S are called the natural variables of internal energy. The *natural variables* of a state function are the variables for which knowledge of how the state function behaves with respect to them allows one to determine all thermodynamic properties of the system. (This will become clearer with examples later on.)

Why did we not introduce equation 4.3 as a spontaneity condition earlier? First, it depends on our definition of entropy, which we did not get to until the previous chapter. Second—and more importantly—it requires a process that is *isentropic*; that is, where $dS = 0$ infinitesimally and $\Delta S = 0$ for the overall process. One can imagine how difficult it must be to perform a process on a system and ensure that the order, on an atomic and molecular level, does not change. (Contrast that with how easy it is to devise a process where dV is zero or, equivalently, ΔV for the entire process equals 0.) To put it bluntly, equation 4.3 is not a very useful spontaneity condition.

Since $dH = dU + d(pV)$, we can substitute for dU in equation 4.3:

$$dH - p\,dV - V\,dp + p\,dV - T\,dS \leq 0$$

For clarity, we are dropping the "ext" label on the pressure variable. The two $p\ dV$ terms cancel to give us

$$dH - V\,dp - T\,dS \leq 0$$

for a spontaneous change. If this change were to occur under conditions of constant pressure and constant entropy, then dp and dS both equal 0, so the spontaneity condition becomes

$$(dH)_{p,S} \leq 0 \tag{4.4}$$

Again, this is not a useful spontaneity condition unless we can keep the process isentropic. Because p and S must be constant in order for the enthalpy change to act as a spontaneity condition, p and S are the natural variables for enthalpy. Equation 4.4 does suggest why many spontaneous changes are exothermic, however. Many processes occur against a constant pressure: that of the atmosphere. Constant pressure is half of the requirement for enthalpy changes to dictate spontaneity. However, it is not sufficient, because for many processes the entropy change is not zero.

Notice a certain trend. Equation 4.1, the spontaneity condition for entropy, states that the entropy change is positive for spontaneous processes. That is, entropy *increases.* On the other hand, the spontaneity conditions for both internal energy and enthalpy, both measures of the energy of a system, require that the change is less than zero: the energy of the system *decreases* in spontaneous changes. Changes toward increased entropy and decreased energy are generally spontaneous *if the proper conditions are met.* However, we still lack a specific spontaneity test for constant pressure and temperature, our most useful experimental conditions.

Example 4.1

State whether or not the following processes can be labeled spontaneous under the following conditions.

a. A process in which ΔH is positive at constant V and p

b. An isobaric process in which ΔU is negative and ΔS is 0

c. An adiabatic process in which ΔS is positive and the volume does not change

d. An isobaric, isentropic process in which ΔH is negative

Solution

a. Spontaneity requires that ΔH be negative if pressure and entropy are constant. Since we do not know the constraints on p and S, there is no requirement that this process *must* be spontaneous.

b. An isobaric process has $\Delta p = 0$. We are also given a negative ΔU and $\Delta S = 0$. Unfortunately, the negative ΔU spontaneity condition requires an isochoric (that is, $\Delta V = 0$) condition. Therefore, we cannot say that this process *must* be spontaneous.

c. An adiabatic process implies $q = 0$, and with volume not changing we have $\Delta V = 0$; therefore $w = 0$ and thus $\Delta U = 0$. The constant U and V allow us to apply the strict entropy spontaneity test: if $\Delta S > 0$, the process is spontaneous. Since we are given that ΔS is positive, this process must be spontaneous.

d. Isobaric and isentropic imply $\Delta p = \Delta S = 0$. These are the proper variables for using the enthalpy spontaneity test, which requires that ΔH be less than zero. This is in fact the case, so this process must be spontaneous.

Note that in the above example, all of the processes *may* be spontaneous. However, only the last two *must* be spontaneous by the laws of thermodynamics as we know them. The difference between "may" and "must" is important for science. Science recognizes that anything *might* occur. It focuses, however, on what *will* occur. These spontaneity conditions help us determine what will occur.

4.3 The Gibbs Free Energy and the Helmholtz Energy

We now define two more energies. The definition of the *Helmholtz energy, A*, is

$$A \equiv U - TS \tag{4.5}$$

The infinitesimal dA is therefore equal to

$$dA = dU - T\,dS - S\,dT$$

which becomes, for a reversible process,

$$dA = -S\,dT - p\,dV$$

where we have used the definition of dU and the entropy for a reversible process as substitutions. Parallel to the above conclusions regarding dU and dH, their natural variables, and spontaneity, we state that the natural variables of A are T and V, and that for an isothermal, isochoric process,

$$(dA)_{T,V} \leq 0 \tag{4.6}$$

is sufficient to ensure the spontaneity of a process. Again, the "equal to" part of the sign applies to processes that occur reversibly. This definition has some application, since some chemical and physical processes do occur under conditions of constant volume (for example, bomb calorimetry).

We also define the *Gibbs energy*, or the *Gibbs free energy, G*, as

$$G \equiv H - TS \tag{4.7}$$

The infinitesimal dG is

$$dG = dH - T\,dS - S\,dT$$

Substituting for the definition of dH and again assuming a reversible change, we get

$$dG = -S\,dT + V\,dp$$

This equation implies certain natural variables, namely T and p, such that the following spontaneity condition is

$$(dG)_{T,p} \leq 0 \tag{4.8}$$

This is the spontaneity condition we have been looking for! We therefore make the following, perhaps premature, statements. Under conditions of constant pressure and temperature:

$$\begin{aligned}
&\text{If } \Delta G < 0\text{:} \quad \text{the process is spontaneous}\\
&\text{If } \Delta G > 0\text{:} \quad \text{the process is not spontaneous}\\
&\text{If } \Delta G = 0\text{:} \quad \text{the system is at equilibrium}
\end{aligned} \tag{4.9}$$

Since G (and A) are state functions, these statements reflect the fact that $\int dG = \Delta G$, not G.

The state functions U, H, A, and G are the only independent energy quantities that can be defined using p, V, T, and S. It is important to note that the only type of work we are considering at this point is pressure-volume work. If other forms of work are performed, then they must be included in the definition of dU. (Usually, they appear as $dw_{\text{non-}pV}$. We will consider one type of non-pV work in a later chapter.)

Furthermore, it must be understood that the condition $\Delta G < 0$ defines only spontaneity, not speed. A reaction may be thermodynamically favorable but might proceed at a snail's pace. For example, the reaction

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (\ell)$$

has a very negative ΔG. However, hydrogen gas and oxygen gas can coexist in an isolated system for millions of years before all of the reactant gas has converted into liquid water. At this point, we cannot address the speed of the reaction. We can address only whether it can occur spontaneously.


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Figure 4.1 Hermann Ludwig Ferdinand von Helmholtz (1821–1894), German physicist and physiologist. In addition to studying various aspects of physiology including sight and hearing, Helmholtz made important contributions to the study of energy. He was one of the first people to clearly enunciate what became the first law of thermodynamics.

The Helmholtz energy is named after the German physician and physicist Hermann Ludwig Ferdinand von Helmholtz (Figure 4.1). He is known for the first detailed, specific enunciation of the first law of thermodynamics in 1847. The Gibbs free energy is named for Josiah Willard Gibbs, an American mathematical physicist (Figure 4.2). In the 1870s, Gibbs took the principles of thermodynamics and applied them mathematically to chemical reactions. In doing so, Gibbs established that the thermodynamics of heat engines was also applicable to chemistry.

The usefulness of the Helmholtz energy, A, can be demonstrated by starting with the first law:

$$dU = dq + dw$$

Since $dS \geq dq/T$, we can rewrite the equation above as

$$dU - T\,dS \leq dw$$

If $dT = 0$ (that is, for an isothermal change), this can be written as

$$d(U - TS) \leq dw$$

Since the quantity inside the parentheses is the definition of A, we can substitute:

$$dA \leq dw$$

which we integrate to get

$$\Delta A \leq w \tag{4.10}$$

This says that the isothermal change in Helmholtz energy is less than or, for reversible changes, equal to the work done by the system on the surroundings. Since work done *by* the system has a negative value, equation 4.10 means that the ΔA of an isothermal process is the maximum *amount* of work a system can do on the surroundings. The connection between work and the Helmholtz energy is the reason that Helmholtz energy is represented by A. It comes from the German word *Arbeit*, meaning "work."

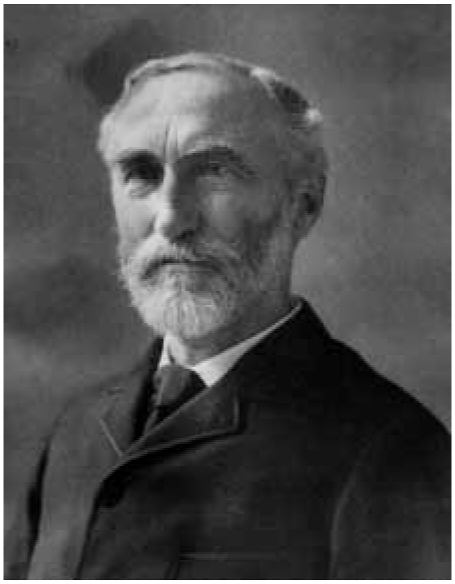
Photo by Gen. Stab. Lit. Anst, AIP Emilio Segrè Visual Archives

Figure 4.2 Josiah Willard Gibbs (1839–1903), American physicist. Gibbs applied the mathematics of thermodynamics to chemical reactions in a rigorous fashion, thereby extending the applicability of thermodynamics from engines to chemistry. However, his work was so much over the heads of his contemporaries that it took almost 20 years for his contributions to be recognized.

A similar expression can be derived for the Gibbs free energy, but using a slightly different understanding of work. So far, we have always discussed work as pV work, work performed by expanding gases against external pressures. This is not the only kind of work. Suppose we define a sort of work that is non-pV work. We can write the first law of thermodynamics as

$$dU = dq + dw_{pV} + dw_{\text{non-}pV}$$

Making the same substitution for $dS \geq dq/T$, and also substituting for the definition of pV work, we get

$$dU + p\,dV - T\,dS \leq dw_{\text{non-}pV}$$

If temperature and pressure are constant (the crucial requirements for a useful G state function), then we can rewrite the differential as

$$d(U + pV - TS) \leq dw_{\text{non-}pV}$$

$U + pV$ is the definition of H. Substituting:

$$d(H - TS) \leq dw_{\text{non-}pV}$$

Also, $H - TS$ is the definition of G:

$$dG \leq dw_{\text{non-}pV}$$

which we can integrate to get

$$\Delta G \leq w_{\text{non-}pV} \tag{4.11}$$

That is, when non-pV work is performed, ΔG represents a limit. Again, since work performed by a system is negative, ΔG represents the maximum amount of non-pV work a system can perform on the surroundings. For a reversible process, the change in the Gibbs free energy is equal to the non-pV work of the process. Equation 4.11 will become important to us in Chapter 8, when we discuss electrochemistry and electrical work.

Example 4.2

Calculate the change in the Helmholtz energy for the reversible isothermal compression of 1 mole of an ideal gas from 100.0 L to 22.4 L. Assume that the temperature is 298 K.

Solution

The process described is the third step in a Carnot-type cycle. Since the process is reversible, the equality relationship $\Delta A = w$ applies. Therefore we need to calculate the work for the process. The work is given by equation 2.7:

$$w = -nRT \ln \frac{V_f}{V_i}$$

Substituting for the various values:

$$w = -(1\text{ mol})\left(8.314\,\frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298\text{ K})\ \ln\left(\frac{22.4\text{ L}}{100.0\text{ L}}\right)$$

$$w = 3610\text{ J}$$

Since for this reversible process $\Delta A = w$, we have

$$\Delta A = 3610\text{ J}$$

Since many processes can be made to occur isothermally (or at least returned to their original temperatures), we can develop the following expressions for ΔA and ΔG:

$$A = U - TS$$

$$dA = dU - T\,dS - S\,dT$$

$$dA = dU - T\,dS \quad \text{for an isothermal change}$$

or, integrating:

$$\Delta A = \Delta U - T\,\Delta S \tag{4.12}$$

Similarly, for the Gibbs free energy:

$$G = H - TS$$

$$dG = dH - T\,dS - S\,dT$$

$$dG = dH - T\,dS \quad \text{for an isothermal change}$$

We integrate to get

$$\Delta G = \Delta H - T\,\Delta S \tag{4.13}$$

Both equations 4.12 and 4.13 are for isothermal changes. They also allow us to calculate ΔA or ΔG if changes in other state functions are known.

Just as we can determine ΔU, ΔH, and ΔS for chemical processes using a Hess's-law approach, we can also determine ΔG and ΔA values for chemical reactions using a products-minus-reactants scheme. Because ΔG is a more useful state function, we focus on that. We define *free energies of formation* $\Delta_f G$ similarly to the enthalpies of formation, and tabulate those. If the $\Delta_f G$ values are determined at standard thermodynamic conditions, we use the ° superscript and label them $\Delta_f G°$. We can then determine the ΔG of a reaction, $\Delta_{rxn} G$, just like we did the enthalpies of reactions. However, with ΔG we have two ways to calculate the free energy change for a reaction. We can use the $\Delta_{rxn} G$ values and a products-minus-reactants approach, *or* we can use equation 4.13. The choice of which to use depends on the information given (or the information you are able to get). Ideally, both approaches should give you the same answer.

Note that the above paragraph implies that $\Delta_f G$ for elements in their standard states is exactly zero. The same is true for $\Delta_f A$. This is because a formation reaction is defined as the formation of a chemical species from its constituent chemical elements in their standard states.

Example 4.3

Determine $\Delta_{rxn} G$ (25°C = 298.15 K) for the following chemical reaction using both methods for determining $\Delta_{rxn} G$, and show that they yield the same answer. Assume standard conditions. Appendix 2 in the back of the book lists the various thermodynamic data.

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (\ell)$$

Solution

The following data were obtained from Appendix 2:

	H_2 (g)	O_2 (g)	H_2O (ℓ)
$\Delta_f H$, kJ/mol	0	0	−285.83
S, J/mol·K	130.68	205.14	69.91
$\Delta_f G$, kJ/mol	0	0	−237.13

We begin by calculating $\Delta_{rxn} H$:

$$\Delta_{rxn} H = 2(-285.83) - (2 \cdot 0 + 1 \cdot 0)$$

$$\Delta_{rxn} H = -571.66\ \text{kJ}$$

Now, we calculate $\Delta_{rxn} S$:

$$\Delta_{rxn} S = 2(69.91) - (2 \cdot 130.68 + 205.14)$$

The 2s are from the stoichiometry of the balanced chemical reaction. We get

$$\Delta_{\text{rxn}}S = -326.68 \text{ J/K}$$

(Is this reasonable, knowing what you should know about entropy?) In combining $\Delta_{\text{rxn}}H$ and $\Delta_{\text{rxn}}S$, we need to make the units compatible. We convert $\Delta_{\text{rxn}}S$ into kilojoule-containing units:

$$\Delta_{\text{rxn}}S = -0.32668 \text{ kJ/K}$$

Using equation 4.13, we calculate $\Delta_{\text{rxn}}G$:

$$\Delta G = \Delta H - T\,\Delta S$$

$$\Delta G = -571.66 \text{ kJ} - (298.15 \text{ K})(-0.32668 \text{ kJ/K})$$

Notice that the K temperature units cancel in the second term. Both terms have the same units of kJ, and we get

$$\Delta G = -474.26 \text{ kJ}$$

using equation 4.13. Using the idea of products-minus-reactants, we use the $\Delta_f G$ values from the table to get

$$\Delta_{\text{rxn}}G = 2(-237.13) - (2 \cdot 0 + 0) \text{ kJ}$$

$$\Delta_{\text{rxn}}G = -474.26 \text{ kJ}$$

This shows that *either* way of evaluating ΔG is appropriate.

4.4 Natural Variable Equations and Partial Derivatives

Now that we have defined all independent energy quantities in terms of p, V, T, and S, we summarize them in terms of their natural variables:

$$dU = T\,dS - p\,dV \tag{4.14}$$

$$dH = T\,dS + V\,dp \tag{4.15}$$

$$dA = -S\,dT - p\,dV \tag{4.16}$$

$$dG = -S\,dT + V\,dp \tag{4.17}$$

These equations are important because when the behaviors of these energies on their natural variables are known, *all thermodynamic properties of the system can be determined.*

For example, consider the internal energy, U. Its natural variables are S and V; that is, the internal energy is a function of S and V:

$$U = U(S, V)$$

As discussed in the last chapter, the overall change in U, dU, can be separated into a component that varies with S and a component that varies with V. The variation of U with respect to S only (that is, V is kept constant) is represented as $(\partial U/\partial S)_V$, the partial derivative of U with respect to S at constant V. This is simply the slope of the graph of U plotted against the entropy, S. Similarly, the variation of U as V changes but S remains constant is represented by $(\partial U/\partial V)_S$, the partial derivative of U with respect to V at constant S. This is the slope of the graph of U plotted versus V. The overall change in U, dU, is therefore

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

But from the natural variable equation, we know that

$$dU = T\,dS - p\,dV$$

If we compare these two equations, the terms multiplying the dS must be equal, as must the terms multiplying the dV. That is,

$$\left(\frac{\partial U}{\partial S}\right)_V dS = T\,dS$$

$$\left(\frac{\partial U}{\partial V}\right)_S dV = -p\,dV$$

We therefore have the following expressions:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{4.18}$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \tag{4.19}$$

Equation 4.18 states that the change in internal energy as the entropy changes at constant volume equals the temperature of the system. Equation 4.19 shows that the change in internal energy as the volume changes at constant entropy equals the negative of the pressure. What fascinating relationships! It means that we do not have to actually measure the change in internal energy versus volume at constant entropy—if we know the pressure of the system, the negative value of it equals that change. Since these changes represent slopes of plots of internal energy versus entropy or volume, we know what those slopes are for our system. So, if we know how U varies with S and V, we also know T and p for our system.

Furthermore, many such partial derivatives can be constructed that cannot be determined experimentally. (Example: Can you construct an experiment in which the entropy remains constant? That can sometimes be extremely difficult to guarantee.) Equations like 4.18 and 4.19 eliminate the need to do that: they tell us mathematically that the change in internal energy with respect to volume at constant entropy equals the negative of the pressure, for example. There is no need to measure internal energy versus volume. All we need to measure is the pressure.

Finally, in many derivations, partial derivatives like these will show up. Equations like 4.18 and 4.19 allow us to substitute simple state variables for more complicated partial derivatives. This will be extremely useful in our further development of thermodynamics and accounts partially for its real power.

Example 4.4

Show that the expression on the left-hand side of Equation 4.18 yields units of temperature.

Solution

The units of U are J/mol, and the units of entropy are J/mol·K. Changes in U and S are also described using those units. Therefore, the units on the derivative (which is a change in U divided by a change in S) are

$$\frac{\text{J/mol}}{\text{J/mol·K}} = \frac{1}{1/\text{K}} = \text{K}$$

which is a unit of temperature.

Other relationships can be derived from the other natural variable equations. From dH:

$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{4.20}$$

$$\left(\frac{\partial H}{\partial p}\right)_S = V \tag{4.21}$$

From dA:

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \tag{4.22}$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -p \tag{4.23}$$

and from dG:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \tag{4.24}$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{4.25}$$

If we know that G is a function of p and T, and we know how G varies with p and T, we also know S and V. Also, knowing G and how it varies with p and T, we can determine the other state functions. Since

$$H = U + pV$$

and

$$G = H - TS$$

we can combine the two equations to get

$$U = G + TS - pV$$

Substituting from the partial derivatives in terms of G (that is, equations 4.24 and 4.25), we see that

$$U = G - T\left(\frac{\partial G}{\partial T}\right)_p - p\left(\frac{\partial G}{\partial p}\right)_T$$

The differential form of this equation is

$$dU = dG - \left(\frac{\partial G}{\partial T}\right)_p dT - \left(\frac{\partial G}{\partial p}\right)_T dp \tag{4.26}$$

We already know dG, and by knowing the two partial derivatives, we can determine U as a function of T and p. Expressions for the other energy state functions can also be determined. The point is, if we know the values for the proper changes in one energy state function, we can use all of the equations of thermodynamics to determine the other changes in energy state functions.

Example 4.5

What is the expression for H, assuming one knows the behavior of G (that is, the partial derivatives in equations 4.24 and 4.25)?

Solution

We can use the equation

$$G = H - TS$$

to get H:

$$H = G + TS$$

If we know how G behaves with respect to its natural variables, we know $(\partial G/\partial T)_p$. This partial derivative is equal to $-S$, so we can substitute to get

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_p$$

which gives us H.

It is worth stating again how useful the natural variable equations are. If we know how any one of the energies varies in terms of its natural variables, we can use the various definitions and equations from the laws of thermodynamics to construct expressions for *any other energy.* The mathematics of thermodynamics is becoming powerful indeed.

4.5 The Maxwell Relationships

The equations involving partial derivatives of the thermodynamic energies can be taken a step further. However, some definitions are necessary.

We have repeatedly made the point that some thermodynamic functions are state functions, and that changes in state functions are independent of the exact path taken. In other words, the change in a state function depends only on the initial and final conditions, not on how the initial conditions became the final conditions.

Consider this in terms of the natural variable equations. They all have two terms, a change with respect to one state variable, and a change with respect to the other state variable. For instance, the natural variable equation for dH is

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp \tag{4.27}$$

where the overall change in H is separated into a change as the entropy S varies, and a change as the pressure p varies. The idea of path-independent changes in state functions means that it does not matter which change occurs first. It does not matter in what order the partial derivatives in H occur. As long as both of them change from designated initial values to designated final values, the overall change in H has the same value.

There is a mathematical parallel to this idea. If you have a mathematical "state function" that depends on two variables $F(x, y)$, then you can determine the overall change in F by setting up a "natural variable" equation for the overall change in F as

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy \tag{4.28}$$

The function $F(x, y)$ changes with respect to x and with respect to y. Suppose you were interested in determining the simultaneous change of F with respect to x and y; that is, you wanted to know the *second* derivative of F with respect to x and y. In what order do you perform the differentiation? Mathematically, it does not matter. This means that the following equality exists:

$$\left[\frac{\partial}{\partial x}\left(\frac{\partial F}{\partial y}\right)_x\right]_y = \left[\frac{\partial}{\partial y}\left(\frac{\partial F}{\partial x}\right)_y\right]_x \tag{4.29}$$

The derivative with respect to x of the derivative of F with respect to y is equal to the derivative with respect to y of the derivative of F with respect to x. If this is the case, then the original differential dF in equation 4.28 satisfies one requirement of an *exact differential*: the value of the multiple differential does not depend on the order of differentiation.* Equation 4.29 is known as the *cross-derivative equality requirement* of exact differentials. In the application of the double derivatives in equation 4.29 to real thermodynamic equations, the partial derivatives may have some other expression, as the following example shows.

Example 4.6

Is the following expression considered an exact differential?

$$dT = \frac{p}{R}\,dV + \frac{V}{R}\,dp$$

Solution

Using equation 4.28 as a template, we can figure by analogy that

$$\left(\frac{\partial T}{\partial V}\right)_p = \frac{p}{R}$$

and that

$$\left(\frac{\partial T}{\partial p}\right)_V = \frac{V}{R}$$

Taking the derivative of the first partial with respect to p, we get

$$\frac{\partial}{\partial p}\left(\frac{\partial T}{\partial V}\right)_p = \frac{1}{R}$$

and taking the derivative of the second partial with respect to V we get

$$\frac{\partial}{\partial V}\left(\frac{\partial T}{\partial p}\right)_V = \frac{1}{R}$$

By definition, the original differential is an exact differential. Therefore, it doesn't matter in which order we differentiate $T(p, V)$, since the double derivative gives us the same value either way.

In the evaluation of exact differentials, the order of differentiation does not matter. For state functions, the path of change does not matter. All that matters is the difference between the initial and final conditions. We submit that the conditions are parallel and that the conclusions are transferable: the differential forms of the natural variable equations for the thermodynamic energies are exact differentials. Therefore, the two ways of taking the mixed second derivatives of U, H, G, and A must be equal. That is,

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right)_p\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)_S\right]_p \tag{4.30}$$

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*This is equivalent to saying that the value of an integral of a state function is path-independent, an idea used in Chapter 2.

from equation 4.29. Similarly, for the other energies:

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V \tag{4.31}$$

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T\right]_V \tag{4.32}$$

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)_T\right]_p = \left[\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right)_p\right]_T \tag{4.33}$$

For each of these relationships, we know the inside partial derivative on both sides of the equations: they are given in equations 4.18–4.25. Substituting for the inside partial derivatives from equation 4.30, we get

$$\left(\frac{\partial}{\partial p}T\right)_S = \left(\frac{\partial}{\partial S}V\right)_p$$

or rather,

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \tag{4.34}$$

This is an extremely useful relationship, as we no longer need to measure the change in volume with respect to entropy at constant pressure: it equals the isentropic change in temperature with respect to pressure. Notice that we have lost any direct relationship to any energy.

Using equations 4.31–4.33, we can also derive the following expressions:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{4.35}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{4.36}$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \tag{4.37}$$

Equations 4.34–4.37 are called *Maxwell relationships* or *Maxwell relations*, after the Scottish mathematician and physicist James Clerk Maxwell (Figure 4.3), who first presented them in 1870. (Although the derivation of equations 4.34–4.37 may seem straightforward now, it wasn't until that time that the basics of thermodynamics were understood well-enough for someone like Maxwell to derive these expressions.)

The Maxwell relationships are extremely useful for two reasons. First, all of them are generally applicable. They are not restricted to ideal gases, or even just gases. They apply to solid and liquid systems as well. Second, they express certain relationships in terms of variables that are easier to measure. For example, it might be difficult to measure entropy directly and determine how entropy varies with respect to volume at constant temperature. The Maxwell relationship in equation 4.36 shows that we don't have to measure it directly. If we measure the change in pressure with respect to temperature at constant volume, $(\partial p/\partial T)_V$, we know $(\partial S/\partial V)_T$. They are equal. The Maxwell relationships are also useful in deriving new equations that we can apply to thermodynamic changes in systems, or in determining the values of changes in state functions that might be difficult to measure directly by experiment. The following examples use the same Maxwell relationship in two different ways.

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Figure 4.3 James Clerk Maxwell (1831–1879), Scottish mathematician. Maxwell made many important contributions before his untimely death just before his 48th birthday. Among them is the Maxwell theory of electromagnetism, which even today forms the basis of electrical and magnetic behavior. He also contributed to the kinetic theory of gases and the development of the second law of thermodynamics. He was one of the few people to understand Gibbs's work.

Example 4.7

What is $(\partial S/\partial V)_T$ for a gas that follows a van der Waals equation of state?

Solution

The Maxwell relationship in equation 4.36 shows that $(\partial S/\partial V)_T$ is equal to $(\partial p/\partial T)_V$. Using the van der Waals equation,

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

Taking the derivative of p with respect to T at constant volume gives

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V - nb}$$

Therefore, by Maxwell's relationships,

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V - nb}$$

We do not need to measure the entropy changes experimentally. We can get the isothermal change in entropy versus volume from the van der Waals parameters.

Example 4.8

In Chapter 1, we showed that

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa}$$

where α is the expansion coefficient and κ is the isothermal compressibility. For mercury, $\alpha = 1.82 \times 10^{-4}$/K and $\kappa = 3.87 \times 10^{-5}$/atm at 20°C. Determine how entropy changes with volume under isothermal conditions at this temperature.

Solution

The derivative of interest is $(\partial S/\partial V)_T$, which by equation 4.36 is equal to $(\partial p/\partial T)_V$. Using the expansion coefficient and the isothermal compressibility:

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{1.82 \times 10^{-4}/\text{K}}{3.87 \times 10^{-5}/\text{atm}} = 4.70\ \frac{\text{atm}}{\text{K}}$$

These do not seem to be appropriate units for entropy and volume. However, if we note that

$$\frac{\text{atm}}{\text{K}} \cdot \frac{101.32\ \text{J}}{\text{L}\cdot\text{atm}} = 101.32\ \frac{\text{J/K}}{\text{L}}$$

we can convert our answer into more identifiable units and find that

$$\left(\frac{\partial S}{\partial V}\right)_T = 476\ \frac{\text{J/K}}{\text{L}}$$

4.6 Using Maxwell Relationships

The Maxwell relationships can be extremely useful in deriving other equations for thermodynamics. For example, since

$$dH = T\,dS + V\,dp$$

then if we hold T constant and divide everything by dp, we get

$$\left(\frac{dH}{dp}\right)_T \equiv \left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V$$

Measuring the change in entropy with respect to pressure is difficult, but using a Maxwell relationship we can substitute some other expression. Since $(\partial S/\partial p)_T$ equals $-(\partial V/\partial T)_p$, we get

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \tag{4.38}$$

where we have switched the order of the terms. Why is this equation useful? Because once we know the equation of state (for example, the ideal gas law), we know V, T, and how V varies with T at constant pressure—and we can use that information to calculate how the enthalpy varies with pressure at constant temperature, all without having to measure the enthalpy.

The enthalpy derivative in equation 4.38 can be used with the Joule-Thomson coefficient, μ_{JT}. Recall that by the cyclic rule of partial derivatives,

$$\begin{aligned}\mu_{\mathrm{JT}} &= -\left(\frac{\partial T}{\partial p}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_p\left(\frac{\partial H}{\partial p}\right)_T \\ &= -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T\end{aligned}$$

We can now substitute for the differential $(\partial H/\partial p)_T$ from equation 4.38 and get

$$\begin{aligned}\mu_{\mathrm{JT}} &= -\frac{1}{C_p}\left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] \\ &= \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]\end{aligned} \tag{4.39}$$

and now we can calculate the Joule-Thomson coefficient of a gas if we know its equation of state and its heat capacity. Equation 4.39 does not require any knowledge of the enthalpy of the system, beyond its heat capacity at constant pressure. These are just two examples of how useful the Maxwell relationships are.

Example 4.9

Use equation 4.39 to determine the value of μ_{JT} for an ideal gas. Assume molar quantities.

Solution

An ideal gas has the ideal gas law as its equation of state:

$$p\overline{V} = RT$$

In order to evaluate equation 4.39, we need to determine $(\partial \overline{V}/\partial T)_p$. We rewrite the ideal gas law as

$$\overline{V} = \frac{RT}{p}$$

and can now evaluate $(\partial\overline{V}/\partial T)_p$:

$$\left(\frac{\partial\overline{V}}{\partial T}\right)_p = \frac{R}{p}$$

Substituting:

$$\mu_{\mathrm{JT}} = \frac{1}{C_p}\left(T\frac{R}{p} - \overline{V}\right) = \frac{1}{C_p}\left(\frac{RT}{p} - \overline{V}\right)$$

But RT/p equals $\overline{V}$, according to the ideal gas law. Substituting:

$$\mu_{\mathrm{JT}} = \frac{1}{C_p}(\overline{V} - \overline{V}) = \frac{1}{C_p}(0) = 0$$

which shows once again that the Joule-Thomson coefficient for an ideal gas is exactly zero.

Example 4.10

Starting with the natural variable equation for dU, derive an expression for the isothermal volume dependence of the internal energy, $(\partial U/\partial V)_T$, in terms of measurable properties (T, V, or p) and α and/or κ. *Hint:* you will have to invoke the cyclic rule of partial derivatives (see Chapter 1).

Solution

The natural variable equation for dU is (from equation 4.14)

$$dU = T\,dS - p\,dV$$

In order to get $(\partial U/\partial V)_T$, we hold the temperature constant and divide both sides by dV. We get

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

Now we use a Maxwell relationship and substitute for $(\partial S/\partial V)_T$, which according to Maxwell's relationships equals $(\partial p/\partial T)_V$. Therefore,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

Now we invoke the hint. The definitions for α, κ, and the partial derivative $(\partial p/\partial T)_V$ all use p, T, and V. The cyclic rule for partial derivatives relates the three possible independent partial derivatives of any three variables A, B, C:

$$\left(\frac{\partial A}{\partial B}\right)_C\left(\frac{\partial B}{\partial C}\right)_A\left(\frac{\partial C}{\partial A}\right)_B = -1$$

For the variables p, V, and T, this means that

$$\underbrace{\left(\frac{\partial V}{\partial T}\right)_p}_{= V\alpha}\left(\frac{\partial T}{\partial p}\right)_V\underbrace{\left(\frac{\partial p}{\partial V}\right)_T}_{= -\frac{1}{V}\frac{1}{\kappa}} = -1$$

where we are showing how the coefficients α and κ relate to the derivatives in this cyclic-rule equation. The middle partial derivative involves p and T at constant V, which is what we are trying to substitute for; we substitute and rearrange as follows:

$$(V\alpha)\left(-\frac{1}{V}\frac{1}{\kappa}\right) = -\left(\frac{\partial p}{\partial T}\right)_V$$

where we have brought the partial derivative we need to substitute for to the other side of the equation. In doing so, we get the partial derivative of *pressure* with respect to *temperature*. On the left side, the volumes cancel, and the negative signs on both sides cancel. We gather everything together to get

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa}$$

Substituting into our equation for $(\partial U/\partial V)_T$:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\alpha}{\kappa} - p$$

where we now have what is required: an equation for $(\partial U/\partial V)_T$ in terms of parameters easily measured experimentally: the temperature T, the pressure p, and the coefficients α and κ.

Example 4.10 above actually has an important lesson. The ability to mathematically derive expressions like this—which provide us with quantities in terms of experimentally determined values—is a major talent of the mathematics of thermodynamics. The mathematics of thermodynamics is a useful tool. Yes, it can get complicated. But there is a lot we can know and say about a system using these tools, and ultimately that is part of what physical chemistry is all about.

4.7 Focus on ΔG

We have found how U, H, and S vary with temperature. For the two energies, the changes with respect to temperature are called heat capacities, and we derived several equations for the change in S with respect to temperature (like equation 3.18, $\Delta S = n \cdot \overline{C} \cdot \ln(T_f/T_i)$, or the integral form previous to equation 3.18 for a nonconstant heat capacity). Since we are making the point that G is the most useful energy state function, how does G vary with temperature?

From the natural variable equation for dG, we found one relationship between G and T:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \tag{4.40}$$

As temperature changes, the change in G is equal to the negative of the entropy of the system. Notice the negative sign on the entropy in this equation: it implies that as temperature goes up, the free energy goes down, and vice versa. This might seem intuitively wrong at first glance: an energy goes *down* as the temperature increases? But recall the original definition of the Gibbs free energy: $G = H - TS$. The negative sign in front of the term that includes temperature does indeed imply that as T increases, G will be lower.

There is another expression that relates the temperature-dependence of G, but in a slightly different fashion. If we start with the definition of G:

$$G = H - TS$$

we remember that $-S$ is defined by the partial derivative in equation 4.40. Substituting:

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_p$$

where the minus signs have canceled. We rearrange this by dividing both sides of the equation by T, and get

$$\frac{G}{T} = \frac{H}{T} + \left(\frac{\partial G}{\partial T}\right)_p$$

Now we further rearrange by bringing all terms in G to one side:

$$\frac{G}{T} - \left(\frac{\partial G}{\partial T}\right)_p = \frac{H}{T} \tag{4.41}$$

Although this might look intractable, we will introduce a simplifying substitution in a roundabout way. Consider the expression G/T. The derivative of this with respect to T at constant p is

$$\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p = -\frac{G}{T^2}\left(\frac{\partial T}{\partial T}\right)_p + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p$$

by strict application of the chain rule. $\partial T/\partial T$ equals 1, so this expression simplifies to

$$\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p = -\frac{G}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p$$

If we multiply this expression by $-T$, we get

$$-T \cdot \frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p = \frac{G}{T} - \left(\frac{\partial G}{\partial T}\right)_p$$

Note that the expression on the right side of the equation is the same as the left side of equation 4.41. We can therefore substitute:

$$-T \cdot \frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p = \frac{H}{T}$$

or

$$\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p = -\frac{H}{T^2} \tag{4.42}$$

This is an extremely simple equation, and when expanding our derivation to consider changes in energy, it should not be too difficult to derive, for the overall process:

$$\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)_p = -\frac{\Delta H}{T^2} \tag{4.43}$$

for a physical or chemical process. Equations 4.42 and 4.43 are two expressions of what is called the *Gibbs-Helmholtz equation.* By using substitution [that is, let $u = 1/T$, $du = -(1/T^2)\ dT$, and so on], you can show that equation 4.43 can also be written as

$$\left(\frac{\partial \frac{\Delta G}{T}}{\partial \frac{1}{T}}\right)_p = \Delta H \tag{4.44}$$

The form given in equation 4.44 is especially useful. By knowing ΔH for a process, we know something about ΔG. A plot of $\Delta G/T$ versus $1/T$ would be equal to ΔH as a slope. (Remember that a derivative is just a slope.) Further, if we make the approximation that ΔH is constant over small temperature ranges, we can use equation 4.44 to approximate ΔG at different temperatures, as the following example illustrates.

Example 4.11

By approximating equation 4.44 as

$$\left(\frac{\Delta \frac{\Delta G}{T}}{\Delta \frac{1}{T}}\right)_p \approx \Delta H$$

predict the value of ΔG (100°C, 1 atm) of the reaction

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (\ell)$$

given that ΔG (25°C, 1 atm) $= -474.36$ kJ and $\Delta H = -571.66$ kJ. Assume constant pressure and ΔH.

Solution

First, we should evaluate $\Delta(1/T)$. Converting the temperatures to kelvins, we find that

$$\Delta\frac{1}{T} = \frac{1}{373\ \text{K}} - \frac{1}{298\ \text{K}} = -0.000674/\text{K}$$

Using the approximated form of equation 4.44:

$$\left(\frac{\Delta \frac{\Delta G}{T}}{-0.000674/\text{K}}\right)_p \approx -571.66\ \text{kJ}$$

$$\Delta\frac{\Delta G}{T} = 0.386\ \frac{\text{kJ}}{\text{K}}$$

Writing $\Delta(\Delta G/T)$ as $(\Delta G/T)_{\text{final}} - (\Delta G/T)_{\text{initial}}$, we can use the conditions given to get the following expression:

$$\left(\frac{\Delta G}{373\ \text{K}}\right)_{\text{final}} - \left(\frac{-474.36\ \text{kJ}}{298\ \text{K}}\right)_{\text{initial}} = 0.386\ \frac{\text{kJ}}{\text{K}}$$

$$\Delta G_{\text{final}} = \Delta G\ (100°\text{C}) = -450.\ \text{kJ}$$

This compares to a value of -439.2 kJ obtained by recalculating ΔH (100°C) and ΔS (100°C) using a Hess's-law type of approach. The Gibbs-Helmholtz equation makes fewer approximations and would be expected to produce more accurate values of ΔG.

What is the relationship between pressure and G? Again, we can get an initial answer from the natural variable equations:

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

We can rewrite this by assuming an isothermal change. The partial derivative can be rearranged as

$$dG = V\,dp$$

We integrate both sides of the equation. Because G is a state function, the integral of dG is ΔG:

$$\Delta G = \int_{p_i}^{p_f} V\,dp$$

For ideal gases, we can use the ideal gas law and substitute for V: $V = nRT/p$, so

$$\Delta G = \int_{p_\mathrm{i}}^{p_\mathrm{f}} \frac{nRT}{p}\, dp = \int_{p_\mathrm{i}}^{p_\mathrm{f}} nRT \frac{dp}{p} = nRT \int_{p_\mathrm{i}}^{p_\mathrm{f}} \frac{dp}{p}$$

From calculus, we know that $\int(dx/x) = \ln x$. Applying this to the integral in the above equation and evaluating at the limits, we get

$$\Delta G = nRT \ln \frac{p_\mathrm{f}}{p_\mathrm{i}} \tag{4.45}$$

which is applicable only for isothermal changes.

Example 4.12

What is the change in G for a process in which 0.022 mole of an ideal gas goes from 2505 psi (pounds per square inch) to 14.5 psi at a room temperature of 295 K?

Solution

Direct application of equation 4.45 yields

$$\Delta G = (0.022\ \mathrm{mol})\left(8.314\ \frac{\mathrm{J}}{\mathrm{mol{\cdot}K}}\right)(295\ \mathrm{K}) \ln \frac{14.5\ \mathrm{psi}}{2505\ \mathrm{psi}}$$

$$\Delta G = -278\ \mathrm{J}$$

Would this be considered a spontaneous process? Since the pressure is not kept constant, the strict application of ΔG as a spontaneity condition is not warranted. However, gases do tend to go from high pressure to low pressure, given the opportunity. We might expect that this process is in fact spontaneous.

4.8 The Chemical Potential and Other Partial Molar Quantities

So far, we have focused on changes in systems that are measured in terms of the system's physical variables, like pressure and temperature and volume and the like. But in chemical reactions, substances change their chemical form. We need to begin to focus on the chemical identity of a material and how it might change during the course of a process.

It has been assumed that the number of moles, n, of a substance has remained constant in all of the changes considered so far. All of the partial derivatives should also have an n subscript on the right side to indicate that the amount of material remains constant: for example, $(\partial U/\partial V)_{T,n}$. However, there is no reason that we can't consider a derivative with respect to amount, n.

Because of the importance of the Gibbs free energy in spontaneity considerations, the majority of derivatives with respect to n concern G. The *chemical potential* of a substance, μ, is defined as the change in the Gibbs free energy with respect to amount at constant temperature and pressure:

$$\mu \equiv \left(\frac{\partial G}{\partial n}\right)_{T,p} \tag{4.46}$$

For systems that have more than one chemical component, we will have to give the chemical potential a label (typically a number or a chemical formula) to specify which component. The chemical potential for a single component μ_i assumes that only the amount of the ith component, n_i, varies, and the amounts of all other components n_j, $j \neq i$, remain constant. Equation 4.46 is therefore written

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j(j\neq i)} \tag{4.47}$$

If we want to consider the infinitesimal change in G now, we must broaden it by considering possible changes in amount of substance, too. The general expression for dG now becomes

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n\text{'s}} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n\text{'s}} dp + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j(j\neq i)} dn_i$$

or

$$dG = -S\,dT + V\,dp + \sum_i \mu_i\,dn_i \tag{4.48}$$

where the summation has as many terms as there are different substances in the system. Equation 4.48 is sometimes referred to as the *fundamental equation of chemical thermodynamics,* since it embodies all state variables of conditions and amounts.

The chemical potential μ_i is the first example of a *partial molar quantity.* It expresses the change in a state variable, the Gibbs free energy, versus molar amount. For pure substances, the chemical potential is simply equal to the change in the Gibbs free energy of the system as the amount of material changes. For systems of more than one component, the chemical potential does not equal the change in free energy of the pure material because each component interacts with the other, which affects the total energy of the system. If all components were ideal, this wouldn't happen, and partial molar quantities would be the same for any component in any system.*

Because of the relationships between the various energies defined by thermodynamics, chemical potential can also be defined in terms of the other energies, but with different state variables held constant:

$$\mu_i \equiv \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j(j\neq i)} \tag{4.51}$$

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*Partial molar quantities can be defined for any state variable. For example, the partial molar change in entropy $\overline{S}_i$ is defined as

$$\overline{S}_i = \left(\frac{\partial S}{\partial n_i}\right)_{n_j(j\neq i)} \tag{4.49}$$

and for whatever other conditions remain constant. Similarly, a partial molar volume $\overline{V}_i$ is defined as

$$\overline{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_j(j\neq i)} \tag{4.50}$$

The partial molar volume is an especially useful concept for condensed phases. It is also the reason why the mixing of 1 L of water and 1 L of alcohol yields a solution whose volume is not 2 L (it's a little less than 2 L): from the strict thermodynamic sense, volumes are not directly additive, but *partial molar volumes* are. [Note that partial molar quantities (except for μ) have the same symbolism as molar quantities, that is, the line over the variable. Thus, care should be exercised when using these two quantities.]

$$\mu_i \equiv \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_j(j\neq i)} \tag{4.52}$$

$$\mu_i \equiv \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j(j\neq i)} \tag{4.53}$$

However, given the usefulness of G, the free energy–based definition of μ will be most useful to us.

Chemical potential is a measure of how much a species wants to undergo a physical or chemical change. If two or more substances exist in a system and have different chemical potentials, some process would occur to equalize the chemical potentials. Thus, chemical potential allows us to begin a consideration of chemical reactions and chemical equilibrium. Although we have considered chemical reactions in some examples (mostly from a products-minus-reactants change in energy or entropy), we have not focused on them. This will change in the next chapter.

4.9 Fugacity

We preface our application of thermodynamics to chemical reactions by defining fugacity, a measure of the nonideality of real gases. First, let us justify the need to define such a quantity.

In developing theory, we assume ideal materials, and we have done just that in thermodynamics. For example, the use of the "ideal gas" is common throughout these chapters. However, there is no such thing as a truly ideal gas. Real gases do not obey the ideal gas law and have more complex equations of state.

As expected, the chemical potential of a gas varies with pressure. By analogy to equation 4.45:

$$\Delta G = nRT \ln \frac{p_\mathrm{f}}{p_\mathrm{i}}$$

we might also submit that, because chemical potential is defined in terms of G, we have a similar equation for the change μ for an ideal gas:

$$\Delta\mu = RT \ln \frac{p_\mathrm{f}}{p_\mathrm{i}} \tag{4.54}$$

We can write both of these equations in a different fashion, by recognizing that the Δ signs on G and μ represent a change, so we can write ΔG or $\Delta\mu$ as $G_\mathrm{final} - G_\mathrm{initial}$ or $\mu_\mathrm{final} - \mu_\mathrm{initial}$:

$$G_\mathrm{final} - G_\mathrm{initial} = nRT \ln \frac{p_\mathrm{f}}{p_\mathrm{i}}$$

$$\mu_\mathrm{final} - \mu_\mathrm{initial} = RT \ln \frac{p_\mathrm{f}}{p_\mathrm{i}}$$

Suppose that for both equations, the initial state is some standard pressure, like 1 atmosphere or 1 bar. (1 atm = 1.01325 bar, so very little error is introduced by using the non-SI-standard 1 atm.) We will denote the initial conditions with a ° symbol, and bring the initial energy quantity over to the right side of the equation. The "final" subscripts are deleted, and the equations are now written as G or μ at any pressure p, calculated with respect to $G°$ and $\mu°$ at some standard pressure (that is, 1 atm or 1 bar):

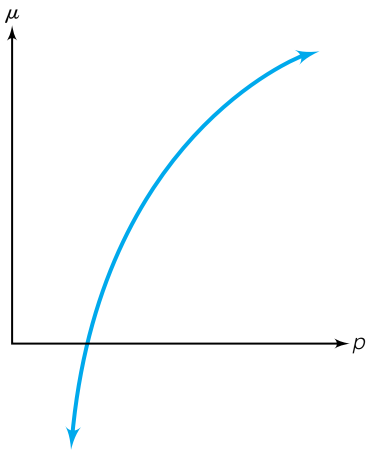


Figure 4.4 An idea of what a plot of the chemical potential μ versus pressure p should look like for an ideal gas.

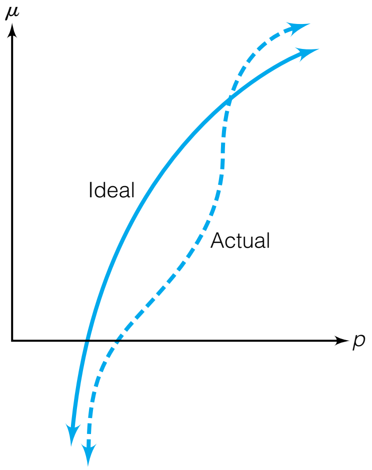


Figure 4.5 For real gases, at high pressures the chemical potential is higher than expected due to intramolecular repulsions. At intermediate pressures, the chemical potential is lower than expected due to intramolecular attractions. At very low pressures, gases tend toward ideal behavior.

$$G = G° + nRT \ln \frac{p}{p°} \tag{4.55}$$

$$\mu = \mu° + RT \ln \frac{p}{p°} \tag{4.56}$$

The second equation shows that the chemical potential varies with the natural logarithm of the pressure. A plot of μ versus p would have a general logarithmic form, as shown in Figure 4.4.

However, measurements on real gases show that the relationship between μ and p isn't so exact. At very, very low gas pressures, all gases approach ideal behavior. At moderate pressures, for a given chemical potential, the pressure is lower than expected. This is because real gas molecules do attract each other slightly, and the measured pressure is lower than ideal. At very high pressures, for a given chemical potential the pressure is higher than expected, because the gas molecules become so densely packed that they begin to repel each other. The actual behavior of the chemical potential versus the real pressure of a gas is shown in Figure 4.5.

For real gases, thermodynamics defines a scaled pressure called *fugacity, f,* as

$$f = \phi \cdot p \tag{4.57}$$

where p is the pressure of the gas and ϕ is called the *fugacity coefficient.* The fugacity coefficient is dimensionless, so fugacity has units of pressure. For real gases, the fugacity is the proper description of how the gas behaves, and so the equation in terms of the chemical potential is better written as

$$\mu = \mu° + RT \ln \frac{f}{p°} \tag{4.58}$$

As the pressure gets lower and lower, any real gas behaves more and more ideally. In the limit of zero pressure, all gases act as ideal gases and their fugacity coefficient equals 1. We write this as

$$\lim_{p\to 0}(f) = p; \qquad \lim_{p\to 0}\phi = 1$$

How do we determine the fugacity experimentally? We can start with the fundamental thermodynamic equation given in equation 4.48:

$$dG = -S\,dT + V\,dp + \sum_i \mu_i\,dn_i$$

For a single component (so that the summation is just one term) undergoing an isothermal process, this becomes

$$dG = V\,dp + \mu\,dn$$

Since dG is an exact differential (see section 4.5), we get the relation $\partial\mu/\partial p = \partial V/\partial n$. The second expression is the partial molar volume of the substance, $\overline{V}$. That is,

$$\frac{\partial\mu}{\partial p} = \overline{V}$$

which leads to

$$d\mu = \overline{V}\,dp$$

For an ideal gas, this would be

$$d\mu_{\text{ideal}} = \overline{V}_{\text{ideal}}\,dp$$

(We will see in a minute why ideal gases are brought up again.) Subtracting these two:

$$d\mu - d\mu_{\text{ideal}} = (\overline{V} - \overline{V}_{\text{ideal}})\,dp$$

where we have factored dp out of both terms on the right. Integrating:

$$\mu - \mu_{\text{ideal}} = \int_0^p (\overline{V} - \overline{V}_{\text{ideal}})\,dp$$

$$\mu - \mu_{\text{ideal}} = \int_0^p \overline{V}\,dp - \int_0^p \overline{V}_{\text{ideal}}\,dp \tag{4.59}$$

If we understand that equation 4.56 gives the chemical potential of an ideal gas μ_{ideal} in terms of pressure and equation 4.58 gives the chemical potential of our real gas μ in terms of fugacity, we can use them to evaluate $\mu - \mu_{\text{ideal}}$:

$$\begin{aligned}\mu - \mu_{\text{ideal}} &= \mu° + RT\ln\frac{f}{p°} - \left(\mu° + RT\ln\frac{p}{p°}\right)\\ &= RT\left(\ln\frac{f}{p°} - \ln\frac{p}{p°}\right)\\ &= RT\ln\frac{f/p°}{p/p°} = RT\ln\frac{f}{p}\end{aligned}$$

Therefore, substituting into the left side of equation 4.59:

$$RT\ln\frac{f}{p} = \int_0^p \overline{V}\,dp - \int_0^p \overline{V}_{\text{ideal}}\,dp$$

Rearranging:

$$\ln\frac{f}{p} = \ln\phi = \frac{1}{RT}\left(\int_0^p \overline{V}\,dp - \int_0^p \overline{V}_{\text{ideal}}\,dp\right) \tag{4.60}$$

This might seem to be a complicated expression, but consider what it is. An integral is an area under a curve. The first integral is the area under a plot of the partial molar volume versus pressure. The second integral is the area under a plot of the ideal molar volume versus pressure. The subtraction of the two integrals, then, is simply *the difference in areas of the two plots between $p = 0$ and some nonzero value of p.* Divide this value by RT and you have the logarithm of the fugacity coefficient ϕ. Fugacities are therefore determined by simply measuring the volumes of known quantities of gases under isothermal conditions and comparing them to the expected ideal volume. Figure 4.6 is an example of what a graphical representation of such an investigation might look like.

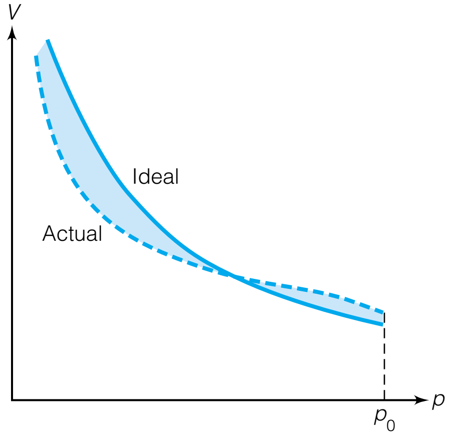


Figure 4.6 A simple way of determining the fugacity coefficient of a real gas is to plot the real volume of the gas at various pressures and compare it to the expected ideal volume of the gas. The fugacity coefficient is related to the difference in the area under the curves (indicated by the shaded portion of the diagram). See equation 4.60.

Equation 4.60 can also be evaluated in terms of the compressibility Z for a real gas. We won't derive it here but simply present the result. (For a derivation see P. W. Atkins and J. de Paulo, *Physical Chemistry*, 7th ed., Freeman, New York, 2002, p. 129.)

$$\ln\phi = \int_0^p \frac{Z-1}{p}\,dp \tag{4.61}$$

If you know the equation of state for a gas and its compressibility in terms of the equation of state, you can substitute for Z in equation 4.61 and evaluate the integral. Or, the compressibility can be plotted and the integral determined by numerically measuring the area under the plot of $(Z - 1)/p$ versus p.

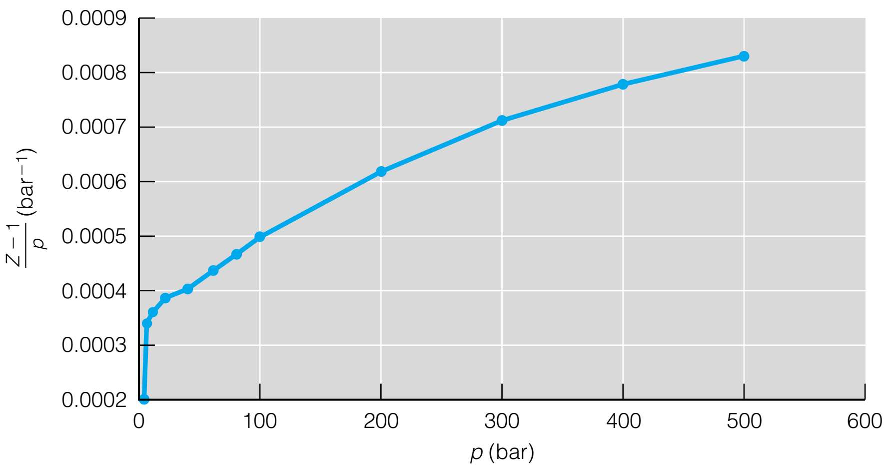


Figure 4.7 On a plot of $(Z - 1)/p$ versus pressure for a real gas, the area under the curve between 0 and some pressure p gives the logarithm of the fugacity coefficient ϕ for the gas at that pressure. The data plotted here are for neon at 150 K.

Figure 4.7 shows such a plot for neon at 150 K. The fugacity of neon at any pressure is the area under this curve from zero to that pressure.

Example 4.13

Calculate the fugacity of 100. atm of argon gas at 600. K assuming its compressibility is adequately represented by the truncated virial equation $Z = 1 + B'p/RT$. B' for Ar at 600 K is 0.012 L/mol (from Table 1.4). Comment on the answer.

Solution

Using equation 4.61:

$$\ln \phi = \int_{0}^{100\text{ atm}} \frac{1 + \frac{B'p}{RT} - 1}{p}\,dp = \int_{0}^{100\text{ atm}} \frac{\frac{B'p}{RT}}{p}\,dp = \int_{0}^{100\text{ atm}} \frac{B'}{RT}\,dp$$

$$= \left.\frac{B'p}{RT}\right|_{0}^{100\text{ atm}} = \frac{B'(100\text{ atm})}{RT}$$

By substituting $B' = 0.012$ L/mol, $R = 0.08205$ L·atm/mol·K and $T = 600$ K, we have

$$\ln \phi = \frac{(0.012\ \frac{\text{L}}{\text{mol}})(100\text{ atm})}{(0.08205\ \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(600\text{ K})} = 0.024$$

Therefore, $\ln \phi = 0.024$, so $\phi = 1.024$. Since $f = \phi p$, this means that $f = 102.$ atm. This argon gas acts as if it had a slightly larger pressure than it actually does. This should be considered approximate, since the virial coefficient B' should be applicable to conditions of 100. atm and 600. K.

Table 4.1 Fugacities of nitrogen gas at 0°C

P (atm)	Fugacity (atm)
1	0.99955
10	9.956
50	49.06
100	97.03
150	145.1
200	194.4
300	301.7
400	424.8
600	743.4
800	1196
1000	1839

Source: G. N. Lewis, M. Randall. *Thermodynamics,* revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, 1961.

To illustrate how fugacity varies with pressure, Table 4.1 lists the fugacities of nitrogen gas. Note how the fugacity almost equals the pressure at $p = 1$ atm, but by the time $p = 1000$ atm, the fugacity is almost twice the pressure.

4.10 Summary

We have introduced the last two energy quantities, the Helmholtz energy and the Gibbs free energy. Both are related to the maximum amount of work a system can perform. When all four energies are written in terms of their natural variables, a startling number of useful relationships can be developed by judicious application of partial derivatives. These derivatives, Maxwell's relationships among them, are very useful because they allow us to express quantities that are difficult to measure directly in terms of changes in state variables that can be easily measured.

We defined the chemical potential μ. It is called a partial molar quantity because it is a partial derivative with respect to the number of moles of material in our system. We can define other partial molar quantities; μ is the first one defined, because of its usefulness as we look into chemical reactions and chemical equilibria.

Finally, we defined fugacity as a necessary description of real gases and showed how we can determine fugacity experimentally in a somewhat simple fashion. It is relatively simple because we have been able to derive a lot of expressions from the basic ideas of thermodynamics and use them to obtain otherwise inaccessible information about our system.

4.2 Spontaneity Conditions

4.1. Explain why conditions for using $\Delta S > 0$ as a strict spontaneity condition imply that ΔU and ΔH both equal zero.

4.2. Explain how the equation

$$\frac{dU + p\,dV}{T} - dS \leq 0$$

is consistent with the idea that spontaneous changes occur with a decrease in energy and an increase in entropy.

4.3. Explain why the spontaneity conditions given in equations 4.3 and 4.4 are in terms of the general derivatives dU and dH and not some partial derivative of U and H with respect to some other state variable.

4.4. Prove that the adiabatic free expansion of an ideal gas is spontaneous.

4.3 Gibbs and Helmholtz Energies

4.5. Derive equation 4.6 from equation 4.5.

4.6. Derive equation 4.8 from equation 4.7.

4.7. The third part of equation 4.9 mentions a condition called equilibrium, in which there is no net change in the state of a system. What are the equilibrium conditions for dU, dH, and dA?

4.8. Calculate ΔA for a process in which 0.160 mole of an ideal gas expands from 1.0 L to 3.5 L against a constant pressure of 880 mmHg at a temperature of 37°C.

4.9. What is the maximum amount of non-pV work that can be done by the reaction

$$2H_2 + O_2 \longrightarrow 2H_2O$$

if $\Delta_f G\ (H_2O) = -237.13$ kJ/mol, and $\Delta_f G\ (H_2) = \Delta_f G\ (O_2) = 0$?

4.10. Consider a piston whose compression ratio is 10:1; that is, $V_f = 10 \times V_i$. If 0.02 mole of gas at 1400 K expands reversibly, what is ΔA for one expansion of the piston?

4.11. When one dives, water pressure increases by 1 atm every 10.55 m of depth. The deepest sea depth is 10,430 m. Assume that 1 mole of gas exists in a small balloon at that depth at 273 K. Assuming an isothermal and reversible process, calculate w, q, ΔU, ΔH, ΔA, and ΔS for the gas after it rises to the surface, assuming the balloon doesn't burst!

4.12. Calculate $\Delta G°$ (25°C) for the following chemical reaction, which is the hydrogenation of benzene to make cyclohexane:

$$C_6H_6\ (\ell) + 3H_2\ (g) \longrightarrow C_6H_{12}\ (\ell)$$

Would you predict that this reaction is spontaneous at constant T and p? Use data in Appendix 2.

4.13. Thermodynamic properties can also be determined for ions. Determine ΔH, ΔS, and ΔG for the following two reactions, which are simply reactions of dissolution:

$$NaHCO_3\ (s) \longrightarrow Na^+\ (aq) + HCO_3^-\ (aq)$$

$$Na_2CO_3\ (s) \longrightarrow 2Na^+\ (aq) + CO_3^{2-}\ (aq)$$

Assume standard conditions (standard concentration is 1 M for ions in aqueous solution), and consult the table of thermodynamic properties in Appendix 2. What similarities and differences are there?

4.14. Calculate ΔG in two different ways for the following dimerization of NO_2:

$$2NO_2\ (g) \longrightarrow N_2O_4\ (g)$$

Are the two values equal?

4.15. Determine ΔG for the following reaction at 0°C and standard pressure:

$$H_2O\ (\ell) \longrightarrow H_2O\ (s)$$

Is the reaction spontaneous? Why are the thermodynamic values from Appendix 2 not strictly applicable to this reaction under these conditions?

4.16. Batteries are chemical systems that can be used to generate electrical work, which is one form of non-pV work. One general reaction that might be used in a battery is

$$M\ (s) + \tfrac{1}{2}X_2\ (s/\ell/g) \longrightarrow MX\ (crystal)$$

where M is an alkali metal and X_2 is a halogen. Using Appendix 2, construct a table that gives the maximum amount of work that a battery can provide if it uses different alkali metals and halogens. Do you know if any of these types of batteries are actually produced?

4.17. Example 4.2 calculated ΔA for one step of a Carnot cycle. What is ΔA for the entire Carnot cycle?

4.4–4.6 Natural Variables, Partial Derivatives, and Maxwell Relationships

4.18. Can C_V and C_p be easily defined using the natural variable expressions for dU and dH? Why or why not?

4.19. Analogous to equation 4.26, what is the expression for U, assuming one knows the behavior of A as it varies with respect to temperature and volume?

4.20. Show that

$$dS = \frac{\alpha}{\kappa}\,dV + \frac{(\partial S/\partial P)_T}{(\partial T/\partial p)_V}\,dT$$

where α is the thermal expansion coefficient and κ is the isothermal compressibility. *Hint:* Write a natural variable expression for dS in terms of V and T and substitute for some of the expressions. You will have to use Maxwell's relationships and the chain rule of partial derivatives.

4.21. Show that the units in equation 4.19 are consistent on either side of the equation.

4.22. Derive equations 4.35–4.37.

4.23. Derivatives of which of the following functions are exact differentials?

(a) $F(x, y) = x + y$

(b) $F(x, y) = x^2 + y^2$

(c) $F(x, y) = x^n y^n$, $n =$ any integer

(d) $F(x, y) = x^m y^n$, $m \neq n$, $m, n =$ any integer

(e) $F(x, y) = y \cdot \sin(xy)$.

4.24. Show that $(\partial S/\partial p)_T = -\alpha V$.

4.25. Starting with the natural variable equation for dH, show that

$$\left(\frac{\partial H}{\partial p}\right)_T = V(1 - \alpha T)$$

4.26. When changes in the conditions of a system are infinitesimal, we use the ∂ or d symbol to indicate a change in a state variable. When they are finite, we use the Δ symbol to indicate the change. Rewrite the natural variable equations 4.14–4.17 in terms of finite changes.

4.27. Equation 4.19 says that

$$\left(\frac{\partial U}{\partial V}\right)_S = -p$$

If we are considering the variation of ΔU, the change in the change of the internal energy, we can write that as (see the previous problem for an analogous argument)

$$\left[\frac{\partial(\Delta U)}{\partial V}\right]_S = -\Delta p$$

Show that this is entirely consistent with the first law of thermodynamics.

4.28. For an isentropic process, what is the approximate change in ΔU if a system consisting of 1.0 mole of gas goes from 7.33 atm and 3.04 L to 1.00 atm and 10.0 L? *Hint:* see the previous problem.

4.29. Use the ideal gas law to demonstrate the cyclic rule of partial derivatives.

4.30. Show that for an ideal gas,

$$\left[C_p - \left(\frac{\partial U}{\partial T}\right)_p - \left(\frac{\partial H}{\partial p}\right)_S \left(\frac{\partial p}{\partial T}\right)_V\right] = 0$$

4.31. Show that

$$\frac{\alpha}{\kappa}\left(\frac{\partial V}{\partial S}\right)_T = 1$$

where α is the expansion coefficient and κ is the isothermal compressibility.

4.32. Evaluate $(\partial U/\partial V)_T$ for an ideal gas. Use the expression from Example 4.10. Does your answer make sense?

4.33. Determine an expression for $(\partial p/\partial S)_T$ for an ideal gas and for a van der Waals gas.

4.7 Focus on ΔG

4.34. Determine the value of the derivative $\{[\partial(\Delta G)]/\partial T\}_p$ for the solid-state reaction

$$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe$$

(*Hint:* see exercise 3.37.)

4.35. Derive the equivalent of the Gibbs-Helmholtz equation, but for the Helmholtz energy A.

4.36. A plot of $1/T$ versus $\Delta G/T$ has what slope?

4.37. A 0.988-mole sample of argon expands from 25.0 L to 35.0 L at a constant temperature of 350 K. Calculate ΔG for this expansion.

4.38. Verify the manipulation of equation 4.41 into equation 4.42. Can you see how the chain rule of derivatives plays an important role in the derivation of the Gibbs-Helmholtz equation?

4.39. Use equation 4.45 as an example and find an expression for ΔA as the volume varies.

4.8 & 4.9 The Chemical Potential and Fugacity

4.40. Why is there no n variable in equation 4.54 like there is in equation 4.45?

4.41. What is the change in the chemical potential of a system if 1 mole of O_2 were added to a system already containing 1 mole of O_2? Probably the best answer is ''no change.'' Why?

4.42. Is μ an extensive or intensive variable? What about the partial molar volume? The partial molar entropy?

4.43. Write the fundamental equation of chemical thermodynamics for a system that contains 1.0 mole of N_2 and 1.0 mole of O_2.

4.44. Calculate the molar change in chemical potential of an ideal gas that expands by 10 times its original volume at **(a)** 100 K, and **(b)** 300 K.

4.45. Calculate the change in chemical potential of an ideal gas that goes from 1.00 atm to 1.00 bar at 273.15 K. How large an absolute amount of change do you think this is?

4.46. Can equation 4.61 be used to calculate ϕ for an ideal gas? Why or why not?

4.47. Which of the following in each pair of systems do you think has the greater chemical potential? **(a)** 1.0 mole of H_2O (ℓ) at 100°C or 1.0 mole of H_2O (g) at 100°C? **(b)** 10.0 g of Fe at 25°C or 10.0 g of Fe at 35°C? **(c)** 25.0 L of air at 1 atm pressure or the same amount of air but compressed isothermally to 100 atm pressure?

4.48. Use equation 4.46 to argue that the absolute chemical potential μ for any substance has a positive value.

4.49. Of helium and oxygen gases, which one do you expect to have a larger deviation from ideality at the same high pressure? Is this the same gas that you would expect to have a larger deviation from ideality at moderate pressure? How about at very low pressure?

4.50. Suppose a gas has an equation of state that resembles a shortened version of the van der Waals equation of state:

$$p(V + nb) = nRT$$

Derive an expression for ϕ for this gas. (See Example 4.13.)

Symbolic Math Exercises

4.51. Use equation 4.39 to determine a numerical value for the Joule-Thomson coefficient, μ_{JT}, for sulfur dioxide, SO_2, at 25°C, assuming that it acts as a van der Waals gas. Van der Waals constants can be found in Table 1.6.

4.52. The following table lists the compressibilities of nitrogen gas, N_2, versus pressure at 300 K.

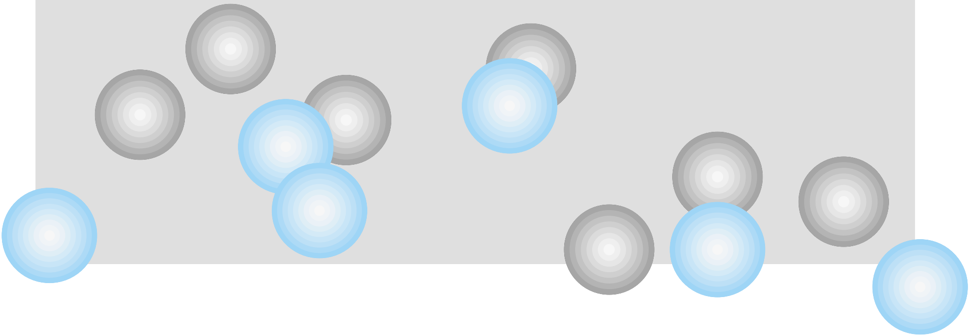
Pressure (bar)	Compressibility
1	1.0000
5	1.0020
10	1.0041
20	1.0091
40	1.0181
60	1.0277
80	1.0369
100	1.0469
200	1.0961
300	1.1476
400	1.1997
500	1.2520

Source: R. H. Perry and D. W. Green, *Perry's Chemical Engineers' Handbook,* 6th ed., McGraw-Hill, New York, 1984).

Evaluate the fugacity coefficient ϕ, and compare the value you get to the value of ϕ found in Example 4.13.

5

Introduction to Chemical Equilibrium



A MAJOR THEME IN CHEMISTRY is *chemical equilibrium:* that point during the course of a chemical reaction where there is no further net change in the chemical composition of the system. One of the triumphs of thermodynamics is that it can be used to understand chemical equilibria.

When you stop and think about it, very few chemical processes are actually *at* chemical equilibrium. Consider the chemical reactions going on in your body's cells. If they were at equilibrium, you wouldn't even be alive! Many chemical reactions that occur on the industrial scale aren't at equilibrium, or else chemical producers wouldn't be making new chemicals for sale.

Then why do we put so much stock in equilibria? For one thing, a system in equilibrium is a system we can understand using thermodynamics. Also, though almost all chemical systems of interest aren't at equilibrium, the idea of equilibrium is used as a starting point. The concept of chemical equilibrium is the very basis for understanding systems that are *not* at equilibrium. An understanding of equilibrium is a central part of understanding chemistry.

5.1 Synopsis

In this introductory chapter, we will define chemical equilibrium. The Gibbs free energy is the energy that is most useful to us, because processes at constant T and p (conditions that are easily established) have dG as a spontaneity condition. Therefore, we will relate the idea of chemical equilibrium to the Gibbs free energy. Chemical reactions go only so far toward completion, and we will define extent as a means of expressing how far a reaction proceeds as pure reactants proceed towards products. We will use extent to help define chemical equilibrium.

Since G is related to the chemical potential, we will see how chemical potential is related to equilibrium. We will see how the equilibrium constant becomes a characteristic for any chemical process. We will find out why solids and liquids do not contribute numerically to values of most equilibrium constants, and why concentrations of solutes in solutions do. Finally, we will consider the fact that the values of equilibrium constants do change with conditions. We will find some straightforward ideas for understanding how pressure and temperature changes affect the value of the equilibrium constant and the extent of the reaction at equilibrium.

5.2 Equilibrium

The rock on the side of the mountain in Figure 5.1a is not at equilibrium because, according to the laws of physics, it should spontaneously roll down the mountain. On the other hand, the rock in Figure 5.1b is at equilibrium because we don't expect any additional, spontaneous change. Rather, if we want to change this system, we will have to put work into the system, but then the change is not spontaneous.

Now consider a chemical system. Think about a 1-cm^3 cube of metallic sodium in a beaker of 100 mL of water. Is the system at equilibrium? Of course not! There ought to be a somewhat violent, spontaneous chemical reaction if we try to put a cubic centimeter of sodium in water. The state of the system as described originally is not at chemical equilibrium. However, it's not a question of gravitational potential energy now. It is a question of chemical reactivity. We say that this Na-in-H_2O system is not at chemical equilibrium.

The sodium metal will react with the water (which is in excess) via the following reaction:

$$2\text{Na (s)} + 2\text{H}_2\text{O} (\ell) \longrightarrow 2\text{Na}^+ \text{(aq)} + 2\text{OH}^- \text{(aq)} + \text{H}_2 \text{(g)}$$

Once that reaction is over, there will be no further change in the chemical identity of the system, and the system is now at chemical equilibrium. In a sense, it is very much like the rock and mountain. The sodium in water represents a rock on the side of a mountain (Figure 5.1a), and the aqueous sodium hydroxide solution (which is an accurate description of the products of the above reaction) represents the rock at the bottom of the mountain (Figure 5.1b).

Consider another chemical system, this one a sample of water, H_2O, and heavy water, D_2O, in a sealed container. (Recall that deuterium, D, is the isotope of hydrogen that has a neutron in its nucleus.) Is this a description of a system at equilibrium? Interestingly, this system is *not* at equilibrium. Over time, water molecules will interact and exchange hydrogen atoms, so that eventually most of the molecules will have the formula HDO—a result that can easily be verified experimentally using, say, a mass spectrometer. (Such reactions, called isotope exchange reactions, are an important part of some modern chemical research.) This process is illustrated in Figure 5.2. Other processes like precipitation of an insoluble salt from aqueous solution are also examples of equilibrium. There is a constant balance between ions

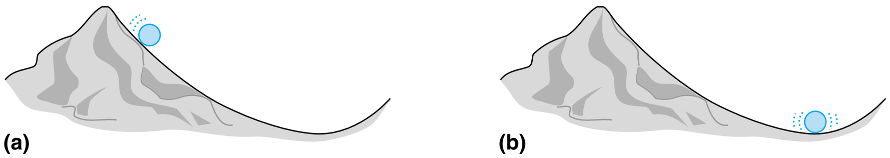


Figure 5.1 (a) A rock on the side of a mountain represents a simple physical system that is not at equilibrium. (b) Now the rock is lying at the bottom of the mountain. The rock is at its minimum gravitational potential energy. This system is at equilibrium.

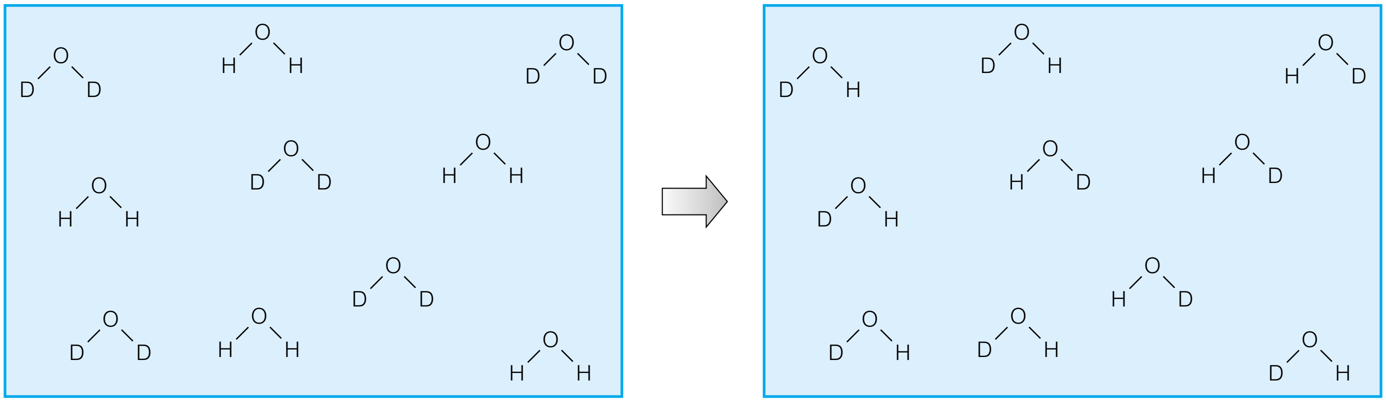


Figure 5.2 Sometimes it is difficult to know whether a system is at chemical equilibrium. An equimolar mixture of H_2O and D_2O—water and heavy water—might appear to be at equilibrium when mixed initially, since both substances are simply water. But in reality, hydrogen exchange occurs to mix the isotopes of hydrogen among the water molecules. At equilibrium, the predominant molecule is HDO.

precipitating from solution and ions dissociating from the solid and going into solution:

$$\mathrm{PbCl_2\ (s) \longrightarrow Pb^{2+}\ (aq) + 2Cl^-\ (aq)}$$

$$\mathrm{Pb^{2+}\ (aq) + 2Cl^-\ (aq) \longrightarrow PbCl_2\ (s)}$$

No net change: chemical equilibrium

The rock on the side of the hill that becomes the rock at the bottom of the hill is an example of an equilibrium, but this is an equilibrium where nothing is happening. This is an example of a *static equilibrium.* Chemical equilibria are different. The chemical reactions are still occurring, but the forward and reverse reactions are occurring at just the same rate so that there is no overall change in the chemical identity of the system. This is called a *dynamic equilibrium.* All chemical equilibria are dynamic equilibria. That is, they are constantly moving, but going nowhere.

Example 5.1

Describe the following situations as either static or dynamic equilibria.

a. The level of water in a fishtank, as the water is constantly passing through a filter

b. A rocking chair that has stopped rocking

c. Acetic acid, a weak acid, that is ionized only to the extent of about 2% in aqueous solution

d. A bank account that maintains an average monthly balance of $1000 despite numerous withdrawals and deposits

Solution

a. Since there is constant motion of the material at equilibrium—the water—this is an example of a dynamic equilibrium.

b. A stopped rocking chair isn't moving at all at the macroscopic level, so this situation is an example of a static equilibrium.

c. The ionization of acetic acid is a chemical reaction, and like all chemical reactions at equilibrium, it is a dynamic one.

d. Because money is moving in and out of the account, even though the average monthly balance maintains the equilibrium amount of \$1000, it is a dynamic equilibrium.

Why does any system come to equilibrium? Consider the rock on the side of the mountain in Figure 5.1a. From physics, we know that gravity is attracting the rock, and the slope of the mountain is not sufficient to counter that attraction and keep the rock from moving. So the rock tumbles down the side of the mountain until it gets to the bottom (Figure 5.1b). At this position, the ground counteracts the force of gravity, and the situation becomes a stable, static equilibrium. One way of considering this system is from the perspective of energy: a rock on the side of the hill has excess gravitational potential energy that it can get rid of by moving down the side of the hill. That is, the rock will spontaneously move to a position that decreases its (gravitational potential) energy. From a physical standpoint, the minimum-energy equilibrium is described in terms of Newton's first law of motion. There are balanced forces acting on the rock, so it remains at rest: at *equilibrium.*

What about chemical reactions? Why do chemical systems eventually reach equilibrium? The answer is analogous to that for the rock: there are balanced "forces" acting on the chemical species in the system. These forces are actually energies—chemical potentials of the different chemical species involved in the system at equilibrium. The next section introduces chemical equilibrium in those terms.

5.3 Chemical Equilibrium

For a chemical reaction occurring in a closed system, species that have some initial chemical identity ("reactants") change to some different chemical identity ("products"). In the previous chapter, we made the point that the Gibbs free energy is dependent on the amount of any substance, and defined the chemical potential as the change in the Gibbs free energy with respect to amount:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j(j\neq i)}$$

Since G varies with each n_i, it should be no surprise that during the course of a chemical process, *the total Gibbs free energy of the entire system changes.*

We now define the extent ξ as a measure of the progress of a reaction. If the number of moles of the ith chemical species in the system at time $t = 0$ is $n_{i,0}$, the extent ξ is given by the expression

$$\xi = \frac{n_i - n_{i,0}}{\nu_i} \tag{5.1}$$

where n_i is the number of moles at some time t and ν_i is the stoichiometric coefficient of the ith chemical species in the reaction. (Remember that ν_i is positive for products and negative for reactants.) The possible numerical values of ξ may vary depending on the initial conditions and the reaction stoichiometry, but at any point in a reaction ξ will have the same value no matter which species is used in equation 5.1.

Example 5.2

The following reaction is set up with the initial amounts of each substance listed below.

$$\begin{array}{ccccc} 6H_2 & + & P_4 & \longrightarrow & 4PH_3 \\ 18.0 \text{ mol} & & 2.0 \text{ mol} & & 1.0 \text{ mol} \end{array}$$

In each of the following scenarios, show that no matter which species is used to determine ξ, the value for ξ is the same.

a. All the P_4 reacts to form products.

b. All the PH_3 reacts to form reactants.

Solution

a. If 2.0 mol P_4 reacts, no P_4 will be left, so $n_{P_4} = 0.0$ mol. Of the H_2, 12.0 mol will have reacted, leaving 6.0 mol H_2 ($n_{H_2} = 6.0$). This produces 8.0 mol PH_3, which in addition to the 1.0 mol initially will give $n_{PH_3} =$ 9.0 mol. Using the definition of ξ and the appropriate values for each chemical species:

$$\xi = \frac{6.0 \text{ mol} - 18.0 \text{ mol}}{-6} = 2.0 \text{ mol} \quad \text{using } H_2$$

$$\xi = \frac{0.0 \text{ mol} - 2.0 \text{ mol}}{-1} = 2.0 \text{ mol} \quad \text{using } P_4$$

$$\xi = \frac{9.0 \text{ mol} - 1.0 \text{ mol}}{+4} = 2.0 \text{ mol} \quad \text{using } PH_3$$

Note that we have used positive or negative values of ν_i, as appropriate, and that extent has units of mol.

b. If all of the PH_3 reacts, n_{PH_3} would be zero and H_2 and P_4 would have gained 1.5 mol and 0.25 mol, respectively. Therefore,

$$\xi = \frac{19.5 \text{ mol} - 18.0 \text{ mol}}{-6} = -0.25 \text{ mol} \quad \text{using } H_2$$

$$\xi = \frac{2.25 \text{ mol} - 2.0 \text{ mol}}{-1} = -0.25 \text{ mol} \quad \text{using } P_4$$

$$\xi = \frac{0.0 \text{ mol} - 1.0 \text{ mol}}{+4} = -0.25 \text{ mol} \quad \text{using } PH_3$$

These examples should convince you that ξ has the same value no matter which species is used and therefore is a consistent way to follow the course of a chemical reaction. In addition, we also see that ξ is positive when a chemical process moves to the right side of the reaction, and negative when it moves to the left side of a reaction.

When a reaction proceeds, the amounts n_i change. The infinitesimal change in each amount, dn_i, can be written in terms of the extent using the relationship in equation 5.1:

$$dn_i = \nu_i \, d\xi \tag{5.2}$$

As the n_i value changes, so does the Gibbs free energy of the system, according to equation 4.48 from the last chapter:

$$dG = -S\,dT + V\,dp + \sum_i \mu_i \, dn_i$$

At constant temperature and pressure, this becomes

$$(dG)_{T,p} = \sum_i \mu_i \, dn_i$$

Substituting for dn_i from equation 5.2, this becomes

$$(dG)_{T,p} = \sum_i \mu_i \nu_i \, d\xi$$

Since the extent variable is the same for all species, we can divide both sides by $d\xi$ to get

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \sum_i \mu_i \nu_i \qquad \textbf{(5.3)}$$

In equations 4.9, we stated that a system was at equilibrium if $\Delta G = 0$ or, equivalently for an infinitesimal process, $dG = 0$. For *chemical equilibrium*, we require that the derivative in equation 5.3, defined as the *Gibbs free energy of reaction* $\Delta_{\text{rxn}}G$, be zero:

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} \equiv \Delta_{\text{rxn}}G = \sum_i \mu_i \nu_i = 0 \quad \text{for chemical equilibrium} \qquad \textbf{(5.4)}$$

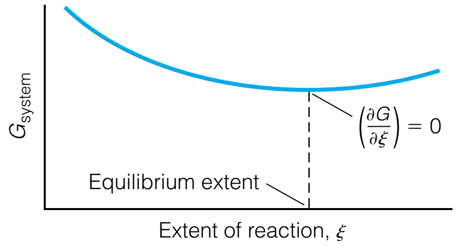


Figure 5.3 Over the course of the reaction (labeled "extent of reaction" on the x-axis), the overall Gibbs free energy comes to a minimum. At this point, the reaction is at chemical equilibrium.

Figure 5.3 illustrates the meaning of equation 5.4. At some extent of reaction, the overall G of the system reaches some minimum value. At that extent, we say that the system has reached chemical equilibrium. (We recognize that derivatives also equal zero at curve *maxima*. However, we will not encounter such situations in our discussion of thermodynamics.)

Example 5.3

The following reaction is set up in a sealed container:

$$2NO_2\ (g) \longrightarrow N_2O_4\ (g)$$

Initially, there are 3.0 mol NO_2 present and no N_2O_4. Write two expressions for the extent of the reaction, and one expression that must be satisfied in order for chemical equilibrium to exist.

Solution

An expression for ξ can be written in terms of either NO_2 or N_2O_4:

$$\xi = \frac{n_{NO_2} - 3.0\ \text{mol}}{-2} = \frac{n_{N_2O_4}}{+1}$$

Chemical equilibrium will exist if the following expression, written in terms of the chemical potentials of NO_2 and N_2O_4, is satisfied:

$$\mu_{N_2O_4} - 2\mu_{NO_2} = 0$$

This expression comes directly from equation 5.4.

Consider a general gas-phase reaction:

$$a\text{A} \longrightarrow b\text{B}$$

For this process, equation 5.4 would be written as

$$\Delta_{\text{rxn}}G = b\mu_{\text{B}} - a\mu_{\text{A}}$$

where a and b are the coefficients of the balanced chemical reaction. The chemical potentials can be written in terms of the standard chemical potential μ° and a term involving a nonstandard pressure. If we assume ideal-gas behavior, we can use equation 4.56 to rewrite the above equation as

$$\Delta_{\text{rxn}}G = b\left(\mu_B^\circ + RT\ln\frac{p_B}{p^\circ}\right) - a\left(\mu_A^\circ + RT\ln\frac{p_A}{p^\circ}\right)$$

We can rearrange this expression algebraically and use properties of logarithms to get

$$\Delta_{\text{rxn}}G = (b\cdot\mu_B^\circ - a\cdot\mu_A^\circ) + RT\ln\frac{(p_B/p^\circ)^b}{(p_A/p^\circ)^a} \tag{5.5}$$

The *standard Gibbs free energy of reaction,* $\Delta_{\text{rxn}}G^\circ$, is defined as

$$\Delta_{\text{rxn}}G^\circ = b\cdot\mu_B^\circ - a\cdot\mu_A^\circ \tag{5.6}$$

As with H and S, we also define $\Delta_f G^\circ$ for formation reactions. Because G is a state function, equation 5.6 can be written in a more useful form in terms of the standard Gibbs free energies of formation:

$$\Delta_{\text{rxn}}G^\circ = b\cdot\Delta_f G^\circ_{\text{prod}} - a\cdot\Delta_f G^\circ_{\text{react}}$$

The quotient $[(p_B/p^\circ)^b]/[(p_A/p^\circ)^a]$ is defined as the *reaction quotient* Q:

$$Q \equiv \frac{(p_B/p^\circ)^b}{(p_A/p^\circ)^a}$$

We therefore write equation 5.5 as

$$\Delta_{\text{rxn}}G = \Delta_{\text{rxn}}G^\circ + RT\ln Q \tag{5.7}$$

The definitions of $\Delta_{\text{rxn}}G^\circ$ and Q can be generalized for any number of reactants and products.

$$\Delta_{\text{rxn}}G^\circ = \sum\Delta_f G^\circ\text{ (products)} - \sum\Delta_f G^\circ\text{ (reactants)} \tag{5.8}$$

$$Q = \frac{\prod\limits_{i\text{ products}} (p_i/p^\circ)^{|\nu_i|}}{\prod\limits_{j\text{ reactants}} (p_j/p^\circ)^{|\nu_j|}} \tag{5.9}$$

Absolute values are used for the ν's because we are writing Q explicitly as a fraction. Using equation 5.8, standard Gibbs free energies of reactions can be determined from the Gibbs free energies of formations. The $\Delta_f G^\circ$ values are tabulated, along with the $\Delta_f H$ values and absolute entropies. The stoichiometry of the chemical reaction must be used when applying equation 5.8, since $\Delta_f G$'s are typically given as molar quantities (that is, as $\overline{\Delta_f G}$).

We should clearly differentiate between $\Delta_{\text{rxn}}G$ and $\Delta_{\text{rxn}}G^\circ$. $\Delta_{\text{rxn}}G$ can have various values, depending on what the exact conditions of the system are and what the extent of the reaction is. $\Delta_{\text{rxn}}G^\circ$, on the other hand, is the change in Gibbs free energy between products and reactants when all reactants and products are in their standard states of pressure, form, and/or concentration (and typically for a specified temperature, like 25°C). $\Delta_{\text{rxn}}G^\circ$ is a characteristic of a reaction, whereas $\Delta_{\text{rxn}}G$ depends on what the exact state of the system is, or what the individual states of the reactants and products are. For instance, equation 5.7 allows us to determine $\Delta_{\text{rxn}}G$ for any reaction under conditions other than standard pressures, as shown in the following example.

Example 5.4

For molar amounts, the standard Gibbs energy of reaction for the following reaction at 25°C is −457.14 kJ:

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (g)$$

In a system where $p_{H_2} = 0.775$ bar, $p_{O_2} = 2.88$ bar, and $p_{H_2O} = 0.556$ bar, determine $\Delta_{rxn}G$. Use 1.00 bar as the standard pressure.

Solution

First, we construct the proper expression for Q. Using equation 5.9, the balanced chemical reaction, and the conditions given:

$$Q = \frac{\left(\dfrac{p_{H_2O}}{1.00\ \text{bar}}\right)^2}{\left(\dfrac{p_{H_2}}{1.00\ \text{bar}}\right)^2\left(\dfrac{p_{O_2}}{1.00\ \text{bar}}\right)} = \frac{\left(\dfrac{0.556\ \text{bar}}{1.00\ \text{bar}}\right)^2}{\left(\dfrac{0.775\ \text{bar}}{1.00\ \text{bar}}\right)^2\left(\dfrac{2.88\ \text{bar}}{1.00\ \text{bar}}\right)}$$

$$Q = 0.179$$

Using equation 5.7 and solving:

$$\Delta_{rxn}G = -457.14\ \text{kJ} + 8.314\ \frac{\text{J}}{\text{K}}(298\ \text{K})\ (\ln 0.179)\ \frac{1\ \text{kJ}}{1000\ \text{J}}$$

$$\Delta_{rxn}G = -461\ \text{kJ}$$

Note the conversion from joules to kilojoules in the solution. Note that the unit on $\Delta_{rxn}G$ is simply kJ, since we are considering molar stoichiometric amounts of reactants and products. If we want to report $\Delta_{rxn}G$ in terms of unit molar amounts of reactants or products, it would be given as −231 kJ/mol H_2, −461 kJ/mol O_2, or −231 kJ/mol H_2O.

For chemical equilibrium, $\Delta_{rxn}G = 0$. Equation 5.7 becomes

$$0 = \Delta_{rxn}G° + RT \ln Q$$

$$\Delta_{rxn}G° = -RT \ln Q$$

Because $\Delta_{rxn}G°$ has a characteristic value for a chemical process, the value of the reaction quotient Q at equilibrium will have a characteristic value as well. It is called the *equilibrium constant* for the reaction and is given the new symbol K. We therefore write the above equation as

$$\Delta_{rxn}G° = -RT \ln K \qquad \textbf{(5.10)}$$

Since K is defined in terms of pressures of products and reactants at equilibrium, the standard Gibbs free energy of a reaction gives us an idea of what the relative amounts of products and reactions will be when the reaction reaches chemical equilibrium. Large values of K suggest more products than reactants at equilibrium, whereas small values of K suggest more reactants than products. Equilibrium constants are never negative. Using the $\Delta_{rxn}G°$ value from Example 5.4, we can calculate a value of K of 1.3×10^{80}, implying a large amount of product and a minuscule amount of reactants when the reaction reaches equilibrium.

Remember that a chemical equilibrium is a dynamic process. Chemical processes do not stop when the G value of the system has been minimized.

Rather, a forward process is balanced by a reverse process. To emphasize that forward and reverse reactions are occurring simultaneously, the double arrow sign $\rightleftharpoons$ is typically used when writing a reaction, instead of a single arrow.

Equilibrium constants can be used to determine extents of reactions, as shown in the following example.

Example 5.5

For the gas-phase reaction

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{water}}{H_2O} \rightleftharpoons \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethanol}}{C_2H_5OH}$$

the equilibrium constant is 4.00 at 120°C.

a. If you start with 1.00 bar of both ethyl acetate and water in a 10.0-L container, what is the extent of the reaction at equilibrium?

b. What is $\Delta_{rxn}G$ at equilibrium? Explain.

c. What is $\Delta_{rxn}G°$ at equilibrium? Explain.

Solution

a. The following chart shows initial and equilibrium amounts of the substances involved in the equilibrium:

Pressure (bar)	$CH_3COOC_2H_5$	+	H_2O	$\rightleftharpoons$	CH_3COOH	+	C_2H_5OH
Initial	1.00		1.00		0		0
Equilibrium	$1.00 - x$		$1.00 - x$		$+x$		$+x$

The expression for the equilibrium constant can be constructed from the chemical reaction, and the values from the final row of the chart are substituted. We get

$$K = \frac{(p_{CH_3COOH}/p°)(p_{C_2H_5OH}/p°)}{(p_{CH_3COOC_2H_5}/p°)(p_{H_2O}/p°)} = 4.00$$

$$4.00 = \frac{(+x)(+x)}{(1.00 - x)(1.00 - x)} = \frac{x^2}{(1.00 - x)^2}$$

This expression can be expanded and solved algebraically using the quadratic formula. When we do this, we get two numerical answers for x, which are

$$x = 0.667 \text{ bar} \quad \text{or} \quad x = 2.00 \text{ bar}$$

We examine each of those roots, keeping in mind the reality of the situation. If we are starting with only 1.00 bar of reactant, we cannot lose 2.00 bar. Therefore we reject $x = 2.00$ bar as not a physically real answer. So in terms of final amounts of reactants and products, we use the $x = 0.667$ bar as the change in amount to get the equilibrium amounts

$$p_{CH_3COOC_2H_5} = 0.333 \text{ bar} \qquad p_{H_2O} = 0.333 \text{ bar}$$

$$p_{CH_3COOH} = 0.667 \qquad p_{C_2H_5OH} = 0.667 \text{ bar}$$

The extent of the reaction at equilibrium can be calculated using any of the reaction species, after converting the amounts to moles. Using H_2O and the ideal gas law:

$$n_{H_2O,init} = 0.306 \text{ mol} \qquad n_{H_2O,equil} = 0.102 \text{ mol}$$

$$\xi = \frac{0.102 \text{ mol} - 0.306 \text{ mol}}{-1}$$

$$\xi = 0.204 \text{ mol}$$

You should be able to verify the value of ξ using any of the other three substances in the reaction.

b. At equilibrium, $\Delta_{rxn}G$ equals zero. Why? Because that's one way to define equilibrium: the instantaneous change in the Gibbs free energy is zero when the reaction is at equilibrium. This is what the equality means in equations 4.9.

c. $\Delta_{rxn}G°$, on the other hand, is not zero. $\Delta_{rxn}G°$ (note the ° sign) is the difference in the Gibbs free energy when reactants and products are in their standard state of pressure and concentration. $\Delta_{rxn}G°$ is related to the value of the equilibrium constant by equation 5.10:

$$\Delta_{rxn}G° = -RT \ln K$$

Given a temperature of 120°C (393 K) and an equilibrium constant value of 4.00, we can substitute:

$$\Delta_{rxn}G° = -\left(8.314 \frac{\text{J}}{\text{mol·K}}\right)(393 \text{ K})(\ln 4.00)$$

Evaluating:

$$\Delta_{rxn}G° = -4530 \text{ J/mol}$$

Because our equilibrium constant has been defined in terms of partial pressures, we will have to convert to those values if some other unit of amount is used, such as moles or grams. The following example illustrates a more complex problem.

Example 5.6

Molecular iodine dissociates into atomic iodine at relatively moderate temperatures. At 1000 K, for a 1.00-L system that has 6.00×10^{-3} moles of I_2 present initially, the final equilibrium pressure is 0.750 atm. Determine the equilibrium amounts of I_2 and atomic I, calculate the equilibrium constant, and determine ξ if the relevant equilibrium is

$$I_2\text{ (g)} \rightleftharpoons 2I\text{ (g)}$$

Assume ideal-gas behavior under these conditions. Use atm as the standard unit for pressure.

Solution

Since this example is a bit more complicated, let us map out a strategy before we begin. We assume that some of the molecular iodine will dissociate—call the amount x—and the amount of atomic iodine, given by the stoichiometry of the reaction, will be $+2x$. In a volume of 1.00 L at 1000 K, we can use the ideal gas law to determine partial pressures. We have to constrain any possible answer to the fact that $p_{I_2} + p_I$ must equal 0.750 atm.

We can construct a chart for this example:

Amount	I_2	$\rightleftharpoons$	2I
Initial	6.00×10^{-3} mol		0 mol
Equilibrium	$6.00 \times 10^{-3} - x$		$+2x$

These equilibrium amounts are in terms of *moles,* not in terms of pressure. We are given the total pressure at equilibrium as well as the temperature. We can use the ideal gas law to convert the moles of each species into pressures of each species, then sum the pressures and require that this sum equals 0.750 atm. Thus, at equilibrium, we have

Pressure (atm)	I_2	$\rightleftharpoons$	$2I$
Equilibrium	$\frac{(6.00 \times 10^{-3} - x)(0.08205)(1000)}{1.00}$		$\frac{(2x)(0.08205)(1000)}{1.00}$

where we have left the units off the variables for clarity. You should be able to recognize the units that go with each value. These pressures represent the partial pressures of the species at equilibrium for this reaction. We use them in the expression for the equilibrium constant:

$$K = \frac{(p_I/p°)^2}{p_{I_2}/p°}$$

We can substitute the partial pressures into the above expression and get

$$K = \frac{\left(\frac{(2x)(0.08205)(1000)}{1.00}\right)}{\left(\frac{(6.00 \times 10^{-3} - x)(0.08205)(1000)}{1.00}\right)^2}$$

which is subject to the condition that

$$\frac{(6.00 \times 10^{-3} - x)(0.08205)(1000)}{1.00} + \frac{(2x)(0.08205)(1000)}{1.00} = 0.750$$

It is this second equation, where it is understood that the units are atm, that is most immediately solvable. By evaluating each fractional expression, we find that

$$0.4923 - 82.05x + 164.1x = 0.750$$

$$82.05x = 0.258$$

$$x = 3.14 \times 10^{-3}$$

where in the last step we have limited our final answer to three significant figures. If we want the equilibrium amount of I_2 and I atoms, we need to solve the appropriate expressions. For the number of moles of reactants and products, we have

$$\text{mol } I_2 = 6.00 \times 10^{-3} - x = 6.00 \times 10^{-3} - 3.14 \times 10^{-3}$$

$$= 2.86 \times 10^{-3} \text{ mol } I_2.$$

$$\text{mol I} = +2x = 2(3.14 \times 10^{-3}) = 6.28 \times 10^{-3} \text{ mol I}$$

To get the equilibrium partial pressures, in terms of which the equilibrium constant is written, we need to use the following expressions:

$$p_{I_2} = \frac{(2.86 \times 10^{-3})(0.08205)(1000)}{1.00} = 0.235 \text{ atm}$$

$$p_I = \frac{(6.28 \times 10^{-3})(0.08205)(1000)}{1.00} = 0.515 \text{ atm}$$

where again we omit the units for clarity. It is easy to see that the sum of the two partial pressures equals 0.750 atm. The equilibrium constant is calculated using these pressures:

$$K = \frac{(p_{\mathrm{I}}/p^\circ)^2}{p_{\mathrm{I}_2}/p^\circ} = \frac{(0.515)^2}{0.235} = 1.13$$

The value of the equilibrium constant suggests that there is about the same amount of products as reactants. The molar amounts as well as the equilibrium partial pressures also support this.

The extent ξ can be determined from the initial and equilibrium amounts of molecular iodine:

$$\xi = \frac{2.86 \times 10^{-3}\ \mathrm{mol} - 6.00 \times 10^{-3}\ \mathrm{mol}}{-1}$$

$$\xi = 0.00314\ \mathrm{mol}$$

This is consistent with a reaction whose equilibrium positions itself about halfway between pure reactants and pure products.

5.4 Solutions and Condensed Phases

Up to this point the equilibrium constants have been expressed in terms of partial pressures. However, for real gases the fugacities of the species should be used. If the pressures are low enough, the pressures themselves can be used, since at low pressures the pressure is approximately equal to the fugacity. But many chemical reactions involve phases other than the gas phase. Solids, liquids, and dissolved solutes also participate in chemical reactions. How are they represented in equilibrium constants?

We answer this by defining *activity* a_i of a material in terms of its standard chemical potential μ_i° and its chemical potential μ_i under nonstandard pressures:

$$\mu_i = \mu_i^\circ + RT \ln a_i \tag{5.11}$$

Comparison of this equation with equation 4.58 shows that for a real gas, activity is defined in terms of the fugacity as

$$a_{\mathrm{gas}} = \frac{f_{\mathrm{gas}}}{p^\circ} \tag{5.12}$$

Reaction quotients (and equilibrium constants) are more formally written in terms of activities, rather than pressures:

$$Q = \frac{\prod_{i\ \mathrm{products}} a^{|\nu_i|}}{\prod_{j\ \mathrm{products}} a_j^{|\nu_j|}} \tag{5.13}$$

This expression applies no matter what the state of the individual reactant or product.

For condensed phases (that is, solids and liquids) and dissolved solutes, there are different expressions for activity, although the definition from equation 5.11 is the same for all materials. For condensed phases, the activity of a particular phase at a specified temperature and standard pressure is represented by $\mu°_i$. In the last chapter, we found that

$$\left(\frac{\partial \mu_i}{\partial p}\right)_T = \overline{V}_i$$

where $\overline{V}_i$ is the molar volume of the ith material. We rearrange this into

$$d\mu_i = \overline{V}_i\, dp$$

The differential of equation 5.11 at constant temperature is

$$d\mu_i = RT\,(d \ln a_i)$$

Combining the last two equations and solving for $d \ln a_i$:

$$d \ln a_i = \frac{\overline{V}_i\, dp}{RT}$$

Integrating both sides from the standard state of $a_i = 1$ and $p = 1$:

$$\int_1^a d \ln a_i = \int_1^p \frac{\overline{V}_i\, dp}{RT}$$

$$\ln a_i = \frac{1}{RT} \int_1^p \overline{V}_i\, dp$$

If the molar volume $\overline{V}_i$ is constant over the pressure interval (and it usually is to a good approximation unless the pressure changes are severe), this integrates to

$$\ln a_i = \frac{\overline{V}_i}{RT}(p - 1) \qquad \textbf{(5.14)}$$

Example 5.7

Determine the activity of liquid water at 25.0°C and 100 bar pressure. The molar volume of H_2O at this temperature is 18.07 cm^3.

Solution

Using equation 5.14, we set up the following:

$$\ln a_i = \frac{\left(18.07\,\frac{\text{cm}^3}{\text{mol}}\right)\left(\frac{1\text{ L}}{1000\text{ cm}^3}\right)}{\left(0.08314\,\frac{\text{L·bar}}{\text{mol·K}}\right)(298\text{ K})}(100\text{ bar} - 1\text{ bar})$$

A conversion factor between liters and cubic centimeters is included in the numerator. Solving:

$$\ln a_i = 0.0722$$

$$a_i = 1.07$$

Notice that the activity of the liquid is close to 1, even at a pressure that is 100 times that of standard pressure. This is generally true for condensed phases at pressures that are typically found in chemical environments. Therefore, in most cases the activities of condensed phases *can be approximated as 1* and they make no numerical contribution to the value of the reaction quotient or equilibrium constant. Note that this is not the case in conditions of extreme pressures or temperatures.

For chemical species that are dissolved in solution (usually water), activities are defined in terms of the mole fraction:

$$a_i = \gamma_i x_i \tag{5.15}$$

where γ_i is the *activity coefficient*. For solutes, the activity coefficient approaches 1 as the mole fraction approaches zero:

$$\lim_{x_i \to 0} \gamma_i = 1 \qquad \lim_{x_i \to 0} (a_i) = x_i$$

Mole fractions can be related to other defined concentration units. The strictest mathematical relationship is between mole fraction and molality, m_i, and is

$$m_i = \frac{1000 x_i}{(1 - x_i) \cdot M_i}$$

where M_i is the molecular weight of the solute in grams per mole, and the 1000 factor in the numerator is for a conversion between grams and kilograms. For dilute solutions, the mole fraction of the solute is small compared to 1, so the x_i in the denominator can be neglected. Solving for x_i, we get

$$x_i = m_i \cdot \frac{M_i}{1000}$$

Thus, the activity for solutes in dilute solution can be written as

$$a_i = \gamma_i \cdot m_i \cdot \frac{M_i}{1000}$$

Using equation 5.11, we substitute for the activity to get

$$\mu_i = \mu_i^\circ + RT \ln\left(\gamma_i \cdot m_i \cdot \frac{M_i}{1000}\right)$$

Since M_i and 1000 are constants, the logarithm term can be separated into two terms, one incorporating these constants and the other incorporating the activity coefficient and the molality:

$$\mu_i = \mu_i^\circ + RT \ln\left(\frac{M_i}{1000}\right) + RT \ln (\gamma_i \cdot m_i)$$

The first two terms on the right side of the equation can be combined to make a "new" standard chemical potential, which we will designate μ_i^*. The above equation becomes

$$\mu_i = \mu_i^* + RT \ln (\gamma_i \cdot m_i)$$

Comparing this to equation 5.11 gives us a useful redefinition of the activity of dissolved solutes:

$$a_i = \gamma_i \cdot m_i \tag{5.16}$$

Equation 5.16 implies that concentrations can be used to express the effect of dissolved solutes in reaction quotient and equilibrium constant expressions. In order that a_i be unitless, we divide the expression by the standard molal concentration of 1 mol/kg, symbolized by m°:

$$a_i = \frac{\gamma_i \cdot m_i}{m^\circ} \tag{5.17}$$

Because for dilute aqueous concentrations the molality is approximately equal to the molarity, it is not uncommon to write equilibrium concentrations in units of molarity. (In fact, this is how it is usually done in introductory courses.) However, this adds an additional approximation in our expression of reaction quotients and equilibrium constants.

Example 5.8

What is the proper expression for the equilibrium constant, in terms of pressures, for the following chemical equilibrium? Assume that conditions are near standard pressures.

$$\mathrm{Fe_2(SO_4)_3\ (s) \rightleftharpoons Fe_2O_3\ (s) + 3SO_3\ (g)}$$

Solution

The correct expression for the equilibrium constant is

$$K = \frac{(a_{\mathrm{SO_3}})^3 a_{\mathrm{Fe_2O_3}}}{a_{\mathrm{Fe_2(SO_4)_3}}} \approx (a_{\mathrm{SO_3}})^3 \approx \left(\frac{p_{\mathrm{SO_3}}}{p^\circ}\right)^3$$

The other species in the equilibrium are condensed phases and, if we are close to standard pressures, do not affect the numerical value of K.

Example 5.9

What is the proper expression for the equilibrium constant for the following chemical equilibrium in terms of concentration and partial pressures? This equilibrium is partly responsible for the atmospheric production of acid rain.

$$\mathrm{2H_2O\ (\ell) + 4NO\ (g) + 3O_2\ (g) \rightleftharpoons 4H^+\ (aq) + 4NO_3{}^-\ (aq)}$$

Solution

The proper equilibrium expression is

$$K = \frac{\left(\dfrac{\gamma_{\mathrm{H^+}} m_{\mathrm{H^+}}}{m^\circ}\right)^4 \left(\dfrac{\gamma_{\mathrm{NO_3{}^-}} m_{\mathrm{NO_3{}^-}}}{m^\circ}\right)^4}{\left(\dfrac{p_{\mathrm{NO}}}{p^\circ}\right)^4 \left(\dfrac{p_{\mathrm{O_2}}}{p^\circ}\right)^3}$$

As a condensed phase, H_2O (ℓ) does not appear in the expression.

5.5 Changes in Equilibrium Constants

Despite their names, the numerical values of equilibrium constants can vary depending on conditions, usually with varying temperatures. The effects of temperature on equilibria are easy to model. In the last chapter, we derived the Gibbs-Helmholtz equation as

$$\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)_p = -\frac{\Delta H}{T^2}$$

When applied to a chemical reaction under conditions of standard pressure, it can be rewritten it as

$$\frac{\partial}{\partial T}\left(\frac{\Delta_{\mathrm{rxn}} G^\circ}{T}\right)_p = -\frac{\Delta_{\mathrm{rxn}} H^\circ}{T^2}$$

Since $\Delta_{\text{rxn}}G° = -RT \ln K$, we can substitute for $(\Delta_{\text{rxn}}G°/T)$ and get

$$\frac{\partial}{\partial T}(-R \ln K)_p = -\frac{\Delta_{\text{rxn}}H°}{T^2}$$

R is a constant, and the two negative signs cancel. This equation rearranges to yield the *van't Hoff equation:*

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta_{\text{rxn}}H°}{RT^2} \tag{5.18}$$

A qualitative description of the changes in K depends on the sign of the enthalpy of reaction. If $\Delta_{\text{rxn}}H$ is positive, then K increases with increasing T and decreases with decreasing T. Endothermic reactions therefore shift towards products with increasing temperatures. If $\Delta_{\text{rxn}}H$ is negative, increasing temperatures decrease the value of K, and vice versa. Exothermic reactions therefore shift toward reactants with increasing temperatures. Both qualitative trends are consistent with *Le Chatelier's principle*, the idea that equilibria that are stressed will shift in the direction that minimizes the stress.

A mathematically equivalent form of the van't Hoff equation is

$$\frac{\partial \ln K}{\partial(1/T)} = -\frac{\Delta_{\text{rxn}}H°}{R} \tag{5.19}$$

This is useful because it implies that a plot of ln K versus $1/T$ has a slope of $-(\Delta_{\text{rxn}}H°)/R$. Values of $\Delta_{\text{rxn}}H$ can be determined graphically by measuring equilibrium constants versus temperature. (Compare this with the analogous plot of the Gibbs-Helmholtz equation. What differences and similarities are there in the two plots?) Figure 5.4 shows an example of such a plot.

A more predictive form of the van't Hoff equation can be found by moving the temperature variables to one side of equation 5.18 and integrating both sides:

$$d \ln K = \frac{\Delta_{\text{rxn}}H°}{RT^2} dT$$

$$\int_{K_1}^{K_2} d \ln K = \int_{T_1}^{T_2} \frac{\Delta_{\text{rxn}}H°}{RT^2} dT$$

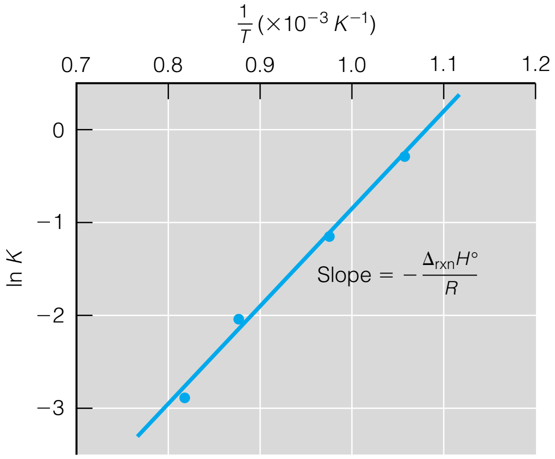


Figure 5.4 Plot of the van't Hoff equation as given in equation 5.19. Plots like this are one graphical way of determining $\Delta_{\text{rxn}}H$.

If $\Delta_{\text{rxn}}H°$ is assumed to not vary over the temperature range, it can be removed from the integral along with R, and the expression becomes

$$\ln\frac{K_2}{K_1}=\frac{\Delta_{\text{rxn}}H°}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\tag{5.20}$$

Using this expression, we can estimate the values of equilibrium constants at different temperatures, knowing the standard enthalpy change. Or, we can estimate the standard enthalpy change knowing the equilibrium constant at two different temperatures, rather than plotting data as suggested by equation 5.19.

Example 5.10

The dimerization of a protein has the following equilibrium constants at the given temperatures: K (4°C) $= 1.3 \times 10^7$, K (15°C) $= 1.5 \times 10^7$. Estimate the standard enthalpy of reaction for this process.

Solution

Using equation 5.20 and remembering to convert our temperatures into kelvins:

$$\ln\frac{1.3\times10^7}{1.5\times10^7}=\frac{\Delta_{\text{rxn}}H°}{8.314\,\frac{\text{J}}{\text{mol}\cdot\text{K}}}\left(\frac{1}{288\text{K}}-\frac{1}{277\text{ K}}\right)$$

Solving for the enthalpy of reaction:

$$\Delta_{\text{rxn}}H° = 8630\text{ J/mol} = 8.63\text{ kJ/mol}$$

How do we rationalize the effect of pressure on an equilibrium? Let us consider a simple gas-phase reaction between NO_2 and N_2O_4:

$$2NO_2 \rightleftharpoons N_2O_4$$

The equilibrium constant expression for this reaction is

$$K=\frac{p_{N_2O_4}/p°}{(p_{NO_2}/p°)^2}$$

If the volume is decreased isothermally, the pressures of both NO_2 and N_2O_4 increase. But the value of the equilibrium constant doesn't change! Because the partial pressure in the denominator is squared as a result of the stoichiometry of the expression, the denominator increases faster relative to the numerator of K as the volume is decreased. In order to compensate, the denominator has to decrease its relative value, and the numerator has to increase its relative value, in order for K to remain constant. In terms of the reaction, this means that the partial pressure of N_2O_4 (the product) goes up and the partial pressure of NO_2 (the reactant) goes down. Generally speaking, the equilibrium shifts toward the side of the reaction that has the lower number of gas molecules; this is the simple expression of the Le Chatelier principle for pressure effects. Inversely, lowering the pressure (for example, by increasing the volume isothermally) will shift the reaction to the side with more gas molecules.

Example 5.11

In Example 5.6, the equilibrium partial pressures of I_2 and I in the gas phase were 0.235 and 0.515 atm, with an equilibrium constant value of 1.13. Suppose the volume were suddenly decreased to 0.500 L at the same temperature, effectively doubling the pressure. The equilibrium then shifts to relieve the stress of the increased pressure. What are the new equilibrium partial pressures? Are the new values consistent with Le Chatelier's principle?

Solution

If the pressure is suddenly decreased to 0.500 L isothermally, then the partial pressures of I_2 and I double to 0.470 and 1.030 atm, respectively. In response to this stress, the equilibrium will shift to re-establish the proper value of the equilibrium constant, which is 1.13. Our initial and equilibrium amounts are:

Pressure (atm)	I_2	$\rightleftharpoons$	**2 I**
Initial	0.470		1.030
Equilibrium	$0.470 + x$		$1.030 - 2x$

Notice in this example that we are working directly with partial pressures. We can substitute the equilibrium partial pressures into the equilibrium constant expression:

$$K = \frac{(p_I/p^\circ)^2}{p_{I_2}/p^\circ} = \frac{(1.030 - 2x)^2}{0.470 + x} = 1.13$$

Using the known value for the equilibrium constant, we can simplify the fraction and multiply through. Simplifying, we get the quadratic equation

$$4x^2 - 5.25x + 0.5298 = 0$$

which has two roots: $x = 1.203$ and $x = 0.110$. The first root is not physically possible because then we would have a negative pressure for I. Thus, $x = 0.110$ is the only acceptable algebraic solution, and our final pressures are

$$p_I = 1.030 - 2(0.110) = 0.810 \text{ atm}$$

$$p_{I_2} = 0.470 + 0.110 = 0.580 \text{ atm}$$

You can verify that these values still give the correct equilibrium constant value. Note that the partial pressure of I has gone down from its original, instantaneously doubled pressure, and that the partial pressure of I_2 has gone up—in accordance with Le Chatelier's principle.

Finally, let us note that if an inert gas is added to a gas-phase equilibrium, one of two things happens depending on the conditions. If the addition of inert gas does *not* change the partial pressures of the gas-phase species (say, the total volume increases instead), the position of the equilibrium does not change. However, if the inert gas pressure does change the partial pressures of the gas-phase species, then the equilibrium position does change as illustrated in Example 5.11.

5.6 Amino Acid Equilibria

As section 2.12 and Example 5.10 show, the principles of thermodynamics are applicable even to the complex reactions that occur in living cells. The topic of equilibrium is also applicable, even though living cells are not isolated or even closed systems.

First, we should point out the seldom-recognized idea that most chemical reactions in cells are not at chemical equilibrium. If an organism or cell were at chemical equilibrium, it would be dead! Nevertheless, the concepts of equilibrium are useful in biochemical reactions. Applications include equilibria of weak acids and bases in aqueous solution, buffer equilibria, and temperature effects on equilibrium, among others.

Amino acids contain the organic acid (or carboxyl) group, –COOH, and a basic amino group, $–NH_2$. The carboxyl group can ionize to $–COO^-$ and H^+, and the amino group can accept an H^+ and become the $–NH_3{}^+$ group. In solid or neutral aqueous phase, the overall neutral amino acid is actually a doubly charged species called a *zwitterion*:*

$$RC(NH_2)COOH \longrightarrow RC(NH_3{}^+)COO^-$$

where R represents the different R groups that distinguish different amino acids. For all amino acids, a series of equilibria between different ions will exist whose equilibrium extents depend on the presence (or absence) of free H^+ ions from other sources (like other acids):

$$RC(NH_3{}^+)COOH \overset{K_1}{\rightleftharpoons} RC(NH_3{}^+)COO^- \overset{K_2}{\rightleftharpoons} RC(NH_2)COO^- \qquad (5.21)$$

The equilibrium constant K_1 is the equilibrium constant for the acid dissociation involved in the ionization of the –COOH group. The equilibrium constant K_2 is the equilibrium constant for the acid dissociation in the loss of H^+ from the $–NH_3{}^+$ group. (The H^+ ions have been left out of equation 5.21 for clarity.) The presence or absence of H^+, though, will dictate the extent of each equilibrium in equation 5.21.

For simplicity's sake, typically the negative logarithm of the K values are tabulated. The negative logarithm (base 10) of the equilibrium constant is labeled the pK (spoken as "pea-kay"):

$$pK \equiv -\log K \qquad (5.22)$$

Values of the pK's for the amino acids in proteins are listed in Table 5.1. When the pH of the solution is such that the amino acid exists as the zwitterionic form, this pH is called the *isoelectric point* of that amino acid. In many cases, the isoelectric point is midway between the two pK's, but for amino acids that have other acidic or basic groups, this is not the case. As Table 5.1 indicates, amino acids have varying behavior in aqueous solution. The point here is that equilibrium processes are important for amino acid chemistry and, by extension, protein chemistry.

Table 5.1 pK values for amino acids

Amino acid	pK_1	pK_2
Alanine	2.34	9.69
Arginine	2.17	9.04
Asparagine	2.02	8.80
Aspartic acid	1.88	9.60
Cysteine	1.96	10.28
Glutamic acid	2.19	9.67
Glutamine	2.17	9.13
Glycine	2.34	9.60
Histidine	1.82	9.17
Isoleucine	2.36	9.60
Leucine	2.36	9.60
Lysine	2.18	8.95
Methionine	2.28	9.21
Phenylalanine	1.83	9.13
Proline	1.99	10.60
Serine	2.21	9.15
Threonine	2.09	9.10
Tryptophan	2.83	9.39
Tyrosine	2.20	9.11
Valine	2.32	9.62

The concept of equilibrium is also important in biochemical processes such as O_2/CO_2 exchange in hemoglobin (for example, see exercise 5.7 at the end of this chapter), the binding of small molecules to DNA strands (as might occur in the transcription process), and the interaction of substrates and enzymes. Temperature effects are important in protein denaturation process. Clearly, the ideas established in this chapter are widely applicable to all chemical reactions, even very complex ones.

5.7 Summary

Chemical equilibrium is defined in terms of a minimum of Gibbs free energy with respect to the extent of a reaction. Because the Gibbs free energy is related to the chemical potential, we can use equations involving chemical potential to derive some equations that relate to equilibrium and nonequilibrium conditions

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*The word *zwitterion* comes from the German word *zwitter*, meaning "hybrid."

of a chemical process. In these expressions, a reaction quotient appears, which is a construction involving the reactants and products of the reaction. For gas-phase reactions, the reaction quotient includes the partial pressures or fugacities of the species. By defining activity, we can expand the reaction quotient to include solids and liquids (although their activities are close enough to 1 that their influence on Q can be ignored) and solutions. For solutions, the molal concentration of solutes is the convenient variable for Q.

At equilibrium, Q has a value that is characteristic of the chemical reaction, because there is a characteristic change in the Gibbs free energy for any particular chemical reaction. This characteristic value of Q is called the equilibrium constant, K. Equilibrium constants are convenient measures of the extent of the reaction at the minimum Gibbs free energy, that is, at equilibrium. Equilibrium constants can change with changes in conditions of a system, but the mathematics of thermodynamics gives us tools to model those changes.

5.2 & 5.3 Equilibrium and Chemical Equilibrium

5.1. Can a battery that has a voltage be considered a system at equilibrium? How about a dead battery? Justify each conclusion.

5.2. What is the difference between a static equilibrium and a dynamic equilibrium? Give examples different from the examples in the text. What is similar for the two types of equilibria?

5.3. Which system in each pair best represents equilibrium species under standard conditions of temperature and pressure? Be prepared to justify your choice.

(a) Rb & H_2O or Rb^+ & OH^- & H_2

(b) Na & Cl_2 or NaCl (crystal)

(c) HCl & H_2O or H^+ (aq) & Cl^- (aq)

(d) C (diamond) or C (graphite)

5.4. *Supersaturated* solutions can be made in which more solute is dissolved in solution than would normally dissolve. These solutions are inherently unstable, however. A seed crystal of calcium acetate, $Ca(C_2H_3O_2)_2$, precipitates the excess solute from a supersaturated solution of calcium acetate. When the excess solute has finished precipitating, a chemical equilibrium is established. Write the chemical equations for that equilibrium, and write the net chemical reaction that occurs overall.

5.5. Following is a chemical reaction between zinc metal and hydrochloric acid in a closed system:

$$\text{Zn (s)} + 2\text{HCl (aq)} \longrightarrow \text{H}_2\text{ (g)} + \text{ZnCl}_2\text{ (aq)}$$

If the initial amounts present are 100.0 g of zinc and 150.0 mL of 2.25 M HCl, determine maximum and minimum possible values of ξ for this reaction.

5.6. The following is a reaction with its initial conditions (amounts of each substance):

$$\begin{array}{ccccc} 6\text{H}_2 & + & \text{P}_4 & \longrightarrow & 4\text{PH}_3 \\ 10.0\text{ mol} & & 3.0\text{ mol} & & 3.5\text{ mol} \end{array}$$

(a) Determine ξ if 1.5 mol of P_4 reacts to make products.

(b) Is it possible for ξ to equal 3 in this case? Why or why not?

5.7. The hemoglobin in blood establishes an equilibrium with oxygen gas very quickly. The equilibrium can be represented as

$$\text{heme} + \text{O}_2 \rightleftharpoons \text{heme}\cdot\text{O}_2$$

where "heme" stands for hemoglobin and "heme·O_2" stands for the hemoglobin-oxygen complex. The value for the equilibrium constant for this reaction is about 9.2×10^{18}. Carbon monoxide also binds with hemoglobin by the following reaction:

$$\text{heme} + \text{CO} \rightleftharpoons \text{heme}\cdot\text{CO}$$

This reaction has an equilibrium constant of 2.3×10^{23}. Which reaction's equilibrium lies farther toward products? Does your answer justify the toxicity of CO?

5.8. 1.00 g of sucrose, $C_{12}H_{22}O_{11}$, dissolves completely in 100.0 mL of water. However, if 200.0 g of sucrose were added to the same amount of water, only 164.0 g would dissolve. Write the equilibria reactions for both systems and comment on their differences.

5.9. If N_2, H_2, and NH_3 gases were contained in a system such that the total pressure were 100.0 bar, then the $p°$ terms in equation 5.9 would be equal to 100.0 bar. True or false? Explain your answer.

5.10. Determine $\Delta_{rxn}G°$ and $\Delta_{rxn}G$ for the following reaction at 25°C, using data in Appendix 2. The partial pressures of the products and reactants are given in the chemical equation.

$$2\text{CO (g, 0.650 bar)} + \text{O}_2\text{ (g, 34.0 bar)} \rightleftharpoons 2\text{CO}_2\text{ (g, 0.0250 bar)}$$

5.11. In atmospheric chemistry, the following chemical reaction converts SO_2, the predominant oxide of sulfur that comes from combustion of S-containing materials, to SO_3, which can combine with H_2O to make sulfuric acid (and thus contribute to acid rain):

$$\text{SO}_2\text{ (g)} + \tfrac{1}{2}\text{O}_2\text{ (g)} \rightleftharpoons \text{SO}_3\ (\ell)$$

(a) Write the expression for K for this equilibrium. **(b)** Calculate the value of $\Delta G°$ for this equilibrium using the $\Delta_f G°$ values in Appendix 2. **(c)** Calculate the value of K for this equilibrium. **(d)** If 1.00 bar of SO_2 and 1.00 bar of O_2 are enclosed in a system in the presence of some SO_3 liquid, in which direction would the equilibrium move?

5.12. Assume that a reaction exists such that equilibrium occurs when the partial pressures of the reactants and products are all 1 bar. If the volume of the system were doubled, all of the partial pressures would be 0.5 bar. Would the system still be at equilibrium? Why or why not?

5.13. Show that $K = K^{1/2}$ if the coefficients of a balanced chemical reaction are all divided by two. Give an example.

5.14. The balanced chemical reaction for the formation of ammonia from its elements is

$$\text{N}_2 + 3\text{H}_2\text{ (g)} \rightleftharpoons 2\text{NH}_3\text{ (g)}$$

(a) What is $\Delta_{rxn}G°$ for this reaction? **(b)** What is $\Delta_{rxn}G$ for this reaction if all species have a partial pressure of 0.500 bar at 25°C? Assume that the fugacities are equal to the partial pressures.

5.15. The answers in exercise 5.14 should show that changing the partial pressure changes the instantaneous $\Delta_{rxn}G$ even though the ratio of partial pressures stays the same (that is, 1:1:1 for standard pressure conditions is equal to 0.5:0.5:0.5 for the given conditions). This suggests the interesting possibility that at some equal partial pressure p of all components, the reaction reverses; that is, the instantaneous $\Delta_{rxn}G$ becomes negative. Determine p for this equilibrium. (You will have to use the properties of logarithms as mentioned in the chapter to find the answer.) Is your answer of value to those who work with gases at high pressures, or at low pressures? What is your reasoning?

5.16. At a high enough temperature, the equilibrium constant is 4.00 for the gas-phase isotope exchange reaction

$$H_2 + D_2 \rightleftharpoons 2\ HD$$

Calculate the equilibrium partial pressures if 0.50 atm of H_2 and 0.10 atm of D_2 were initially present in a closed system. What is the extent of reaction at equilibrium?

5.17. If 0.50 atm of krypton were part of the equilibrium in exercise 5.16, would the value of the equilibrium constant be the same or different if the volume were kept the same? Is this case different from Examples 5.6 and 5.11?

5.18. Nitrogen dioxide, NO_2, dimerizes easily to form dinitrogen tetroxide, N_2O_4:

$$2NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$$

(a) Using data in Appendix 2, calculate $\Delta_{rxn}G°$ and K for this equilibrium.

(b) Calculate ξ for this equilibrium if 1.00 mol NO_2 were present initially and allowed to come to equilibrium with the dimer in a 20.0-L system.

5.19. Another nitrogen-oxygen reaction of some importance is

$$2NO_2\ (g) + H_2O\ (g) \longrightarrow HNO_3\ (g) + HNO_2\ (g)$$

which is thought to be the primary reaction involved in the production of acid rain. Determine $\Delta_{rxn}G°$ and K for this reaction.

5.20. Suppose the reaction in Example 5.5 occurred in a 20.0-L vessel. Would the amounts at equilibrium be different? How about ξ at equilibrium?

5.4 Solutions and Condensed Phases

5.21. Write proper expressions for the equilibrium constant for the following reactions.

(a) $PbCl_2\ (s) \rightleftharpoons Pb^{2+}\ (aq) + 2Cl^-\ (aq)$

(b) $HNO_2\ (aq) \rightleftharpoons H^+\ (aq) + NO_2^-\ (aq)$

(c) $CaCO_3\ (s) + H_2C_2O_4\ (aq) \rightleftharpoons CaC_2O_4\ (s) + H_2O\ (\ell) + CO_2\ (g)$

5.22. The $\Delta_fG°$ of diamond, a crystalline form of elemental carbon, is +2.90 kJ/mol at 25.0°C. Give the equilibrium constant for the reaction

$$C\ (s,\ graphite) \rightleftharpoons C\ (s,\ diamond)$$

On the basis of your answer, speculate on the natural occurrence of diamond.

5.23. The densities of graphite and diamond are 2.25 and 3.51 g/cm^3, respectively. Using the expression

$$\Delta_{rxn}G = \Delta_{rxn}G° + RT \ln \frac{a_{dia}}{a_{gra}}$$

and equation 5.14, estimate the pressure necessary for $\Delta_{rxn}G$ to equal zero. What is the stable high-pressure solid phase of carbon?

5.24. Buckminsterfullerene, C_{60}, is a spherical molecule composed of hexagons and pentagons of carbon atoms reminiscent of a geodesic dome. It is currently the focus of much scientific study. For C_{60}, $\Delta_fG°$ is 23.98 kJ/mol at 25.0°. Write the balanced formation reaction for 1 mole of buckminsterfullerene and calculate the equilibrium constant for the formation reaction.

5.25. The bisulfate (or hydrogen sulfate) anion, HSO_4^-, is a weak acid. The equilibrium constant for the aqueous acid reaction

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

is 1.2×10^{-2}.

(a) Calculate $\Delta G°$ for this equilibrium.

(b) At low concentrations, activity coefficients are approximately 1 and the activity of a dissolved solute equals its molality. Determine the equilibrium molalities of a 0.010-molal solution of sodium hydrogen sulfate.

5.5 Changes in Equilibrium Constants

5.26. For the reaction

$$2Na\ (g) \rightleftharpoons Na_2\ (g)$$

the following values of K have been determined (C. T. Ewing et al., *J. Chem. Phys.* 1967, 71, 473):

T (K)	*K*
900	1.32
1000	0.47
1100	0.21
1200	0.10

From these data, estimate $\Delta_{rxn}H°$ for the reaction.

5.27. For a reaction whose standard enthalpy change is −100.0 kJ, what temperature is needed to double the equilibrium constant from its value at 298 K? What temperature is needed to increase the equilibrium constant by a factor of 10? What if the standard enthalpy change were −20.0 kJ?

5.28. Consider the following equilibrium:

$$2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)$$

What is the effect on the equilibrium of each of the following changes? (You may need to calculate some standard enthalpy or Gibbs free energy changes to answer these.) **(a)** The pressure is increased by decreasing the volume. **(b)** The temperature is decreased. **(c)** The pressure is increased by the addition of nitrogen gas, N_2.

5.29. Show that equations 5.18 and 5.19 are equivalent.

5.6 Amino Acid Equilibria

5.30. Of the amino acids listed in Table 5.1, which one should have an isoelectric point closest to 7, the pH of neutral water?

5.31. Determine the concentrations of the three ionic forms of glycine present if 1.0 mol of glycine is used to make 1.00 L of aqueous solution. $pK_1 = 2.34$, $pK_2 = 9.60$. Do you need to make any other assumptions to simplify the calculation?

Symbolic Math Exercises

5.32. Consider the balanced chemical reaction

$$CH_4\ (g) + Br_2\ (g) \longrightarrow CH_2Br_2\ (g) + 2HBr\ (g)$$

A system starts with 10.0 mol CH_4 and 3.75 mol Br_2, and 0.00 mol of the two products. Plot ξ versus amount of each product and reactant. Comment on the differences in the plot.

5.33. For the gas-phase reaction

$$2H_2 + O_2 \longrightarrow 2H_2O$$

$\Delta_{rxn}G°$ is -457.18 kJ. What does a graph of ΔG versus $\ln Q$ ($\ln Q$ varying from -50 to $+50$) look like at 25°C? Change the temperature and find out if the graph looks substantially different at different temperatures.

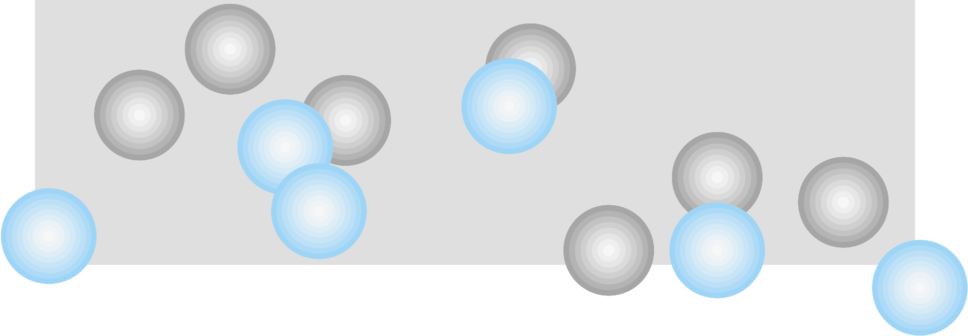
5.34. Simple equilibrium problems can get mathematically complicated when the coefficients are different small whole numbers. For the balanced reaction

$$2SO_3\ (g) \longrightarrow S_2\ (g) + 3O_2\ (g)$$

the equilibrium constant has a value of 4.33×10^{-2} at some elevated temperature. Calculate the equilibrium concentrations of all species if the initial amount of SO_3 were **(a)** 0.150 atm, **(b)** 0.100 atm, **(c)** 0.001 atm.

6

Equilibria in Single-Component Systems



THE PREVIOUS CHAPTER introduced some of the concepts of equilibrium. This chapter and the next will expand on those concepts as we apply them to certain types of chemical systems. Here, we focus on the simplest of systems, those that consist of a single chemical component. It may seem strange that we would spend much effort on such simple systems, but there is a reason. The ideas we develop using simple systems apply to more complicated systems. The more thoroughly the basic concepts are developed, the more easily they can be applied to real systems.

6.1 Synopsis

Very few kinds of equilibria can be considered for single-component systems, but they provide the basis for our understanding of the equilibria of multicomponent systems. First, we will define component and phase. We will use some of the mathematics from the previous chapter to derive new expressions that we can use to understand the equilibria of single-component systems. For such simple systems, graphical methods of illustrating these equilibria—phase diagrams—are useful. We will explore some simple examples of phase diagrams and discuss the information that they provide. Finally, we will introduce a simplifying equation called the Gibbs phase rule, which is useful for multicomponent systems as well.

6.2 A Single-Component System

Suppose you have a system you want to describe thermodynamically. How do you do it? Perhaps most important in your description is *what's in the system;* that is, the components of the system. For our purposes, a *component* is defined as a unique chemical substance that has definite properties. For example, a system composed of pure UF_6 has a single chemical component: uranium hexafluoride. Granted, UF_6 is composed of two elements, uranium and fluorine, but each element lost its individual identity when the compound UF_6 was formed. The phrase "chemically homogeneous" can be used to describe single-component systems.

On the other hand, a mixture of iron filings and sulfur powder is composed of the two components iron and sulfur. The mixture may look like a single component, but a close enough inspection reveals two distinct materials in the system that have their own unique properties. This Fe/S mixture is therefore a *two*-component system. The phrase "chemically inhomogeneous" is used to describe multicomponent systems.

A *solution* is a homogeneous mixture. Examples of solutions include salt water [NaCl (s) dissolved in H_2O] and the alloy brass, which is a solid solution of copper and zinc. Solutions are a little more difficult to consider, because the isolated components might not have the same chemical identity when in solution. For example, NaCl (s) and H_2O (ℓ) are two chemical components, but NaCl (aq) consists of Na^+ (aq) and Cl^- (aq) ions as well as excess H_2O solvent. When we use solutions as an example of a system, we will be explicit in defining the components of the system. Even though they are homogeneous, properties of solutions will not be considered in this chapter.

In this chapter, we are considering single-component systems—that is, systems that have the same chemical composition throughout. However, there is another way to describe the state of the system in addition to its chemical composition. We recognize that matter can exist in different physical forms. A *phase* is a portion of matter that has a uniform physical state and is distinctly separated from other phases. Chemically, we recognize the solid, liquid, and gas phases. We also recognize that one chemical substance may have more than one solid form, and that each form is a different solid phase. Single-component systems can exist in one or more phases simultaneously, and we will apply the concepts of equilibrium from the last chapter to understanding the phase transitions in these systems.

Example 6.1

Identify the number of components and phases that exist in each system. Assume no component other than the ones given exists in each system.

a. A system containing ice and water

b. A 50 : 50 solution of water and ethanol, C_2H_5OH

c. A pressurized tank of carbon dioxide that contains both liquid and gas

d. A bomb calorimeter containing a pellet of benzoic acid, C_6H_5COOH (s), and 25.0 bar of O_2 gas

e. The same bomb calorimeter after the explosion, in which the benzoic acid is converted to CO_2 (g) and H_2O (ℓ), and assuming excess oxygen

Solution

a. Ice water contains H_2O in both solid and liquid forms, so there is a single component and two phases.

b. Both water and ethanol are liquids, so there is one phase of two components.

c. Just like the ice water, the pressurized carbon dioxide with liquid and gas in a tank consists of a single chemical component in two phases.

d. In an unexploded bomb calorimeter, the solid pellet and oxygen gas are two components and two phases.

e. After the explosion, the benzoic acid combusts to make carbon dioxide gas and liquid water. In the presence of excess O_2, there are therefore three components in two phases.

Now we consider something that is usually so obvious to us that we do not really think about it. The stable phase of a single-component system depends on the conditions of the system. Let us use water as an example. When it is cold outside, it might snow (we see solid H_2O), but when it's warmer it rains (we see liquid H_2O). To make spaghetti, we have to boil water (make gaseous H_2O). The temperature of the system determines the stable phase of the H_2O. This idea is obvious to most of us. What might not be so obvious is that the phase of any single-component system depends on *all* of the conditions of the system. Those conditions are the pressure, temperature, volume, and amount of material in the system.

A *phase transition* occurs when a pure component changes from one phase to another. Table 6.1 lists the different types of phase transitions, most of which should already be familiar to you. There are also phase transitions between different solid forms of a chemical component, which is a characteristic called *polymorphism.* For example, elemental carbon exists as graphite or diamond, and the conditions for phase transitions between the two forms are well known. Solid H_2O can actually exist as at least six structurally different solids, depending on the temperature and pressure. We say that water has at least six *polymorphs.* (In application to elements, we use the word *allotrope* instead of polymorph. Graphite and diamond are two allotropes of the element carbon.) In mineral form, calcium carbonate exists either as aragonite or calcite, depending on the crystalline form of the solid.

Table 6.1 Phase transitions[a]

Term	Transition
Melting (or *fusion*)	Solid → liquid
Boiling (or *vaporization*)	Liquid →gas
Sublimation	Solid → gas
Condensation	Gas → liquid
Condensation (or *deposition*)	Gas → solid
Solidification (or *freezing*)	Liquid → solid

[a] There is no specific term for a solid phase → solid phase transition between two solid forms of the same component.

Under most conditions of constant volume, amount, pressure, and temperature, a single-component system has a unique stable phase. For example, a liter of H_2O at atmospheric pressure and 25°C is normally in the liquid phase. However, under the same conditions of pressure but at 125°C, a liter of H_2O would exist as a gas. These are the phases that are thermodynamically stable under these conditions.

For an isolated single-component system having fixed volume and amount, at certain values of pressure and temperature, more than one phase can exist simultaneously in the system. If the state variables of the system are constant, then the system is at equilibrium. Therefore, *it is possible for two or more phases to exist in a system at equilibrium.*

If the system is not isolated but simply closed, then heat can enter or leave the system. In that case, the relative amounts of each phase will change. For example, in a system containing solid dimethyl sulfoxide (DMSO) and liquid DMSO at 18.4°C and atmospheric pressure, when heat is added to the system, some of the solid phase will melt to become part of the liquid phase. The system is still at *chemical* equilibrium, even though the relative amounts of phases are changing (which is a physical change). This is true of other phase transitions as well. At atmospheric pressure and 189°C, liquid DMSO can exist *in equilibrium* with gaseous DMSO. Add or remove heat, and DMSO will go from liquid to gas phase or from gas to liquid phase, respectively, while maintaining a chemical equilibrium.

For a given volume and amount, the temperature at which these equilibria can occur varies with pressure, and vice versa. It is therefore convenient to identify certain benchmark conditions. The *normal melting point* is that temperature at which a solid can exist in equilibrium with its liquid phase at 1 atm pressure.* Because the solid and liquid phases are so condensed, the melting point of single components are affected only by large pressure changes. The

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*We note the disparity that "normal" boiling and melting points are defined in terms of a non-SI unit.

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Figure 6.1 Two different phases of the same component can exist together in equilibrium with each other. However, the conditions at which this can occur are highly specific.

normal boiling point is that temperature at which a liquid can exist in equilibrium with its gas phase at 1 atm. Since the behavior of one of the phases—the gas phase—is strongly dependent on the pressure, boiling points can vary greatly with even small pressure changes. Therefore, we need to be certain that we know the pressure when we discuss a boiling, sublimation, or condensation process.

If the presence of two different phases in a single-component, closed system represents a process at equilibrium, then we can use some of the ideas and equations from the previous chapter. For example, consider the chemical potentials of each phase for, say, a solid-liquid equilibrium as illustrated in Figure 6.1. We are assuming constant pressure and temperature. The natural variable equation for G, equation 4.48, must be satisfied, so we have

$$dG = -S\,dT + V\,dp + \sum_{\text{phases}} \mu_{\text{phase}} \cdot dn_{\text{phase}}$$

At equilibrium, dG is equal to zero at constant T and p. The dT and dp terms in the above equation are also zero. Therefore, for this phase equilibrium, we have

$$\sum_{\text{phases}} \mu_{\text{phase}} \cdot dn_{\text{phase}} = 0 \tag{6.1}$$

For our solid-liquid equilibrium, this expands into two terms:

$$\mu_{\text{solid}} \cdot dn_{\text{solid}} + \mu_{\text{liquid}} \cdot dn_{\text{liquid}} = 0$$

For a single-component system, it should be obvious that if the equilibrium changes infinitesimally, then the amount of change in one phase equals the amount of change in the other phase. However, as one goes down, the other goes up, so there is also a negative numerical relationship between the two infinitesimal changes. We write this mathematically as

$$dn_{\text{liquid}} = -dn_{\text{solid}} \tag{6.2}$$

We can substitute for either of the infinitesimal changes. In terms of the solid phase, we get

$$\mu_{\text{solid}}\, dn_{\text{solid}} + \mu_{\text{liquid}}(-dn_{\text{solid}}) = 0$$

$$\mu_{\text{solid}}\, dn_{\text{solid}} - \mu_{\text{liquid}}\, dn_{\text{solid}} = 0$$

$$(\mu_{\text{solid}} - \mu_{\text{liquid}})\, dn_{\text{solid}} = 0$$

Although the infinitesimal dn_{solid} is indeed infinitesimally small, it is not zero. In order for this equation to equal zero, the expression inside the parentheses must therefore be zero:

$$\mu_{\text{solid}} - \mu_{\text{liquid}} = 0$$

We typically write that at the equilibrium between the solid and liquid phase,

$$\mu_{\text{solid}} = \mu_{\text{liquid}} \tag{6.3}$$

That is, the chemical potentials of the two phases are equal. We expand on this theme and state that *at equilibrium, the chemical potentials of multiple phases of the same component are equal.*

Since we are considering a closed system with a single component, there are two other implicit conditions for a system at equilibrium:

$$T_{\text{phase1}} = T_{\text{phase2}}$$

$$p_{\text{phase1}} = p_{\text{phase2}}$$

If an equilibrium is established and then the temperature or the pressure is changed, the equilibrium must *shift:* that is, the relative amounts of the phases must change until equation 6.3 is re-established.

What if the chemical potentials of the phases are not equal? Then one (or more) of the phases is not the stable phase under those conditions. The phase with the lower chemical potential is the more stable phase. For example, at −10°C, solid H_2O has a lower chemical potential than liquid H_2O, whereas at +10°C, liquid H_2O has a lower chemical potential than solid H_2O. However, at 0°C at normal pressure, both solid and liquid H_2O have the same chemical potential. They can therefore exist together in the same system, at equilibrium.

Example 6.2

Determine whether the chemical potentials of the two phases listed are the same or different. If they are different, state which one is lower than the other.

a. Liquid mercury, Hg (ℓ), or solid mercury, Hg (s), at its normal melting point of −38.9°C
b. H_2O (ℓ) or H_2O (g) at 99°C and 1 atm
c. H_2O (ℓ) or H_2O (g) at 100°C and 1 atm
d. H_2O (ℓ) or H_2O (g) at 101°C and 1 atm
e. Solid lithium chloride, LiCl, or gaseous LiCl at 2000°C and normal pressure (The boiling point of LiCl is about 1350°C.)
f. Oxygen, O_2, or ozone, O_3, at STP

Solution

a. At the normal melting point, both solid and liquid phases can exist in equilibrium. Therefore, the two chemical potentials are equal.
b. At 99°C, the liquid phase of water is the stable phase, so $\mu_{H_2O,\ell} < \mu_{H_2O,g}$.
c. 100°C is the normal boiling point of water, so at that temperature, the chemical potentials are equal.
d. At 101°C, the gas phase is the stable phase for H_2O. Therefore, $\mu_{H_2O,g} < \mu_{H_2O,\ell}$. (See what a difference 2° makes?)
e. Since the stated temperature is above the boiling point of LiCl, the chemical potential of gas-phase LiCl is lower than solid-phase LiCl.
f. Since diatomic oxygen is the stablest allotrope of oxygen, we expect that $\mu_{O_2} < \mu_{O_3}$. Note that this example doesn't involve a phase transition.

6.3 Phase Transitions

Having established that different phases of the same component can exist simultaneously at equilibrium, we might ask what affects that equilibrium. Among other things, the movement of heat into or out of the system affects the equilibrium. Depending on the direction of heat transfer, one phase grows in amount while the other phase simultaneously decreases in amount. This is what happens in a phase transition. Most people are probably aware of the following processes that occur with the stated direction of heat flow:

$$\begin{gathered}
\text{solid} \underset{\text{heat out (exothermic)}}{\overset{\text{heat in (endothermic)}}{\rightleftharpoons}} \text{liquid} \\
\text{liquid} \underset{\text{heat out (exothermic)}}{\overset{\text{heat in (endothermic)}}{\rightleftharpoons}} \text{gas} \\
\text{solid} \underset{\text{heat out (exothermic)}}{\overset{\text{heat in (endothermic)}}{\rightleftharpoons}} \text{gas}
\end{gathered} \tag{6.4}$$

During the phase transition, the temperature of the system remains constant: phase transitions are *isothermal* processes. Only when all of one phase has completely changed to another phase will the heat act to change the temperature of the system. Because each chemical component requires a characteristic amount of heat for a fusion (or melting), vaporization, or sublimation process, we can define heats of fusion, $\Delta_{\text{fus}}H$, heats of vaporization, $\Delta_{\text{vap}}H$, and heats of sublimation, $\Delta_{\text{sub}}H$, for pure compounds. Since these processes usually occur under conditions of constant pressure, these "heats" are in fact enthalpies of fusion, vaporization, or sublimation. Many of these changes are accompanied by a change in volume, which can be large for transitions involving a gas phase.

Enthalpies of phase transitions are formally defined for the endothermic process. Hence they are all positive numbers. But, since each process above occurs under the same conditions except for the direction of heat flow, these enthalpies of phase transition also apply to phase transitions in the opposite direction. That is, the heat of fusion is used for the freezing process as well as the melting process. A heat of vaporization can be used for a vaporization or the reverse condensation process, and so on. For the exothermic processes, the negative of the enthalpy is used, as Hess's law requires us to negate the enthalpy change when we consider the reverse process.

For a phase transition, the amount of heat absorbed or given off is given by the well-known expression

$$q = m \cdot \Delta_{\text{trans}}H \tag{6.5}$$

where m is the mass of the component in the system. We are using the "trans" label to stand for any phase transition: fusion, vaporization, or sublimation. Typically, it is the problem solver's responsibility to understand the inherent direction of heat flow, that is, exothermic or endothermic, and use the appropriate sign on $\Delta_{\text{trans}}H$.

In terms of moles, equation 6.5 is written as

$$q = n \cdot \Delta_{\text{trans}}\overline{H}$$

The units on the enthalpy of phase transition are typically kJ/mol or kJ/g.

A short table of enthalpies of phase transition is given in Table 6.2. Note their units listed in the footnote, and be sure to express the amounts of the components in the appropriate units when working problems.

We must remember that phase transitions themselves are inherently *isothermal*. Furthermore, we have already established that at the melting point or the boiling point of a substance,

$$\mu_{\text{phase1}} = \mu_{\text{phase2}}$$

This implies that for a system where the amount of material is constant and both phases exist in equilibrium,

$$\Delta_{\text{trans}}G = 0 \tag{6.6}$$

This is applicable only to the isothermal phase transition. If the temperature changes from the normal melting or boiling point of the substance, equation 6.6 does not apply. For example, for the isothermal phase transition

$$H_2O\ (\ell,\ 100°\text{C}) \longrightarrow H_2O\ (\text{g},\ 100°\text{C})$$

the ΔG value is zero. However, for the nonisothermal process

$$H_2O\ (\ell,\ 99°\text{C}) \longrightarrow H_2O\ (\text{g},\ 101°\text{C})$$

Table 6.2 Values for enthalpy and entropy of phase transitions[a]

Substance	$\Delta_{fus}H$	$\Delta_{vap}H$	$\Delta_{sub}H$	$\Delta_{fus}S$	$\Delta_{vap}S$	$\Delta_{sub}S$
Acetic acid	11.7	23.7	51.6 (15°C)	40.4	61.9	107.6 (−35 − 10°C)
Ammonia	5.652	23.35		28.93	97.4	
Argon	1.183	6.469			74.8	
Benzene	9.9	30.7	33.6 (1°C)	38.0	87.2	133 (−30 − 5°C)
Carbon dioxide	8.33	15.82	25.23			
Dimethyl sulfoxide	13.9	43.1	52.9 (4°)			
Ethanol	5.0	38.6	42.3 (1°C)		109.8	
Gallium	5.59	270.3	286.2	18.44		
Helium	0.0138	0.0817		4.8	19.9	
Hydrogen	0.117	0.904		8.3	44.6	
Iodine	15.52	41.95	62.42			
Mercury	2.2953	51.9	61.38		92.92	
Methane	0.94	8.2			73.2	91.3 (∼ −190°C)
Naphthalene	19.0	43.3	72.6 (10°C)		82.6	167
Oxygen	0.444	6.820	8.204	8.2	75.6	
Water	6.009	40.66	50.92	22.0	109.1	

Sources: J. A. Dean, ed. *Lange's Handbook of Chemistry,* 14th ed., McGraw-Hill, New York, 1992; D. R. Lide, ed., *CRC Handbook of Chemistry and Physics,* 82nd ed., CRC Press, Boca Raton, Fla., 2001.

[a] All ΔH's are in kJ/mol and all ΔS's are in J/(mol·K). All values are applicable to the normal melting and boiling points of the substances. Sublimation data are applicable to standard temperature unless otherwise noted.

the ΔG value is not zero. This process is not just the phase transition. It includes a change in temperature as well.

One consequence of equation 6.6 comes from the equation for the isothermal ΔG:

$$\Delta G = \Delta H - T\,\Delta S$$

If ΔG is zero for an isothermal phase transition, then we have

$$0 = \Delta_{trans}H - T_{trans} \cdot \Delta_{trans}S$$

Rewriting, we have

$$\Delta_{trans}S = \frac{\Delta_{trans}H}{T_{trans}} \tag{6.7}$$

Since $\Delta_{trans}H$ represents the $\Delta_{vap}H$ and $\Delta_{fus}H$ values that are commonly tabulated, it is relatively easy to calculate the change in entropy that accompanies a phase transition. However, $\Delta_{vap}H$ and $\Delta_{fus}H$ values are usually tabulated as *positive* numbers. This implies an endothermic process. Only fusion and vaporization are endothermic; condensation phase transitions (gas to liquid and gas to solid) and crystallization or solidification phase transitions are *exothermic*. When using equation 6.7 to calculate the change in entropy, the endo- or exothermicity of the process must be determined to get the correct sign on $\Delta_{trans}S$. Example 6.3 illustrates this.

Example 6.3

Calculate the change in entropy for the following phase transitions.

a. One mole of mercury liquid, Hg, freezes at its normal melting point of −38.9°C. The heat of fusion of mercury is 2.33 kJ/mol.

b. One mole of carbon tetrachloride, CCl_4, vaporizes at its normal boiling point of 77.0°C. The heat of vaporization of carbon tetrachloride is 29.89 kJ/mol.

Solution

a. The specific chemical process that is the freezing of mercury is

$$\text{Hg}\ (\ell) \longrightarrow \text{Hg}\ (\text{s})$$

which occurs at −38.9°C or 234.3 K. When the liquid phase goes to the solid phase, heat must be lost, so the process is inherently exothermic. Therefore $\Delta_{\text{trans}}H$ is actually −2.33 kJ/mol, or −2330 J/mol (not the positive 2.33 kJ/mol given for $\Delta_{\text{fus}}H$ for Hg). To determine the entropy change, we have

$$\Delta S = \frac{-2330\ \text{J/mol}}{234.3\ \text{K}} = -9.94\ \frac{\text{J}}{\text{mol·K}}$$

The entropy change is negative, meaning the entropy decreases. This is what's expected for a liquid-to-solid phase transition.

b. The vaporization of carbon tetrachloride is represented by the reaction

$$\text{CCl}_4\ (\ell) \longrightarrow \text{CCl}_4\ (\text{g})$$

which at normal atmospheric pressure occurs at 77.0°C, or 350.2 K. In order to go from the liquid phase to the gas phase, energy must be put into the system, which means that this change is inherently endothermic. Therefore we can use $\Delta_{\text{vap}}H$ directly. For the entropy change, we have

$$\Delta S = \frac{+29{,}890\ \text{J/mol}}{350.2\ \text{K}} = +85.35\ \frac{\text{J}}{\text{mol·K}}$$

It was noted as early as 1884 that many compounds have a $\Delta_{\text{vap}}S$ of around 85 J/mol·K. This phenomenon is called *Trouton's rule.* Deviations from Trouton's rule are marked for substances that have strong intermolecular interactions, like hydrogen bonding. Table 6.2 gives a list of $\Delta_{\text{vap}}H$ and $\Delta_{\text{vap}}S$ values for some compounds. Hydrogen and helium have very small entropies of vaporization. Compounds that have strong hydrogen bonding, like water (H_2O) and ethanol (C_2H_5OH), have higher entropies of vaporization than expected. Table 6.2 also lists $\Delta_{\text{fus}}H$ and $\Delta_{\text{fus}}S$ values for these compounds.

6.4 The Clapeyron Equation

The previous discussion detailed general trends in the behavior of equilibria. In order to get more quantitative, we need to derive some new expressions.

Equation 6.3, when generalized, states that the chemical potential of two phases of the same component are equal at equilibrium:

$$\mu_{\text{phase1}} = \mu_{\text{phase2}}$$

By analogy to the natural variable expression for G, at a constant total amount of substance the infinitesimal change in μ, $d\mu$, as pressure and temperature change infinitesimally is given by the equation

$$d\mu = -\overline{S}\ dT + \overline{V}\ dp \tag{6.8}$$

(Compare this to equation 4.17.) If the multiphase equilibrium experienced an infinitesimal change in T or p, the equilibrium would shift infinitesimally but would still be at equilibrium. This means that the *change* in μ_{phase1} would equal the change in μ_{phase2}. That is,

$$d\mu_{\text{phase1}} = d\mu_{\text{phase2}}$$

and using equation 6.8, we get

$$-\overline{S}_{\text{phase1}}\,dT + \overline{V}_{\text{phase1}}\,dp = -\overline{S}_{\text{phase2}}\,dT + \overline{V}_{\text{phase2}}\,dp$$

Because the temperature change dT and pressure change dp are experienced by both phases simultaneously, there is no need to put labels on them. However, each phase will have its own characteristic molar entropy and molar volume, so each $\overline{S}$ and $\overline{V}$ must have a label to distinguish it. We can rearrange to collect the dp terms and the dT terms on opposite sides:

$$(\overline{V}_{\text{phase2}} - \overline{V}_{\text{phase1}})\,dp = (\overline{S}_{\text{phase2}} - \overline{S}_{\text{phase1}})\,dT$$

We write the differences inside the parentheses as $\Delta\overline{V}$ and $\Delta\overline{S}$, since they represent the changes in molar volume and entropy from phase 1 to phase 2. Substituting,

$$\Delta\overline{V}\,dp = \Delta\overline{S}\,dT$$

which is rearranged to get the following equation:

$$\frac{dp}{dT} = \frac{\Delta\overline{S}}{\Delta\overline{V}} \tag{6.9}$$

This is called the *Clapeyron equation,* after Benoit P. E. Clapeyron, a French engineer who worked out this relationship in 1834. (See Figure 6.2.) The Clapeyron equation relates pressure and temperature changes for all phase equilibria in terms of the changes in molar volumes and entropies of the phases involved. It is applicable to any phase equilibrium. It is sometimes estimated as

$$\frac{\Delta p}{\Delta T} \approx \frac{\Delta\overline{S}}{\Delta\overline{V}} \tag{6.10}$$

One very useful application of the Clapeyron equation is to estimate the pressures necessary to shift phase equilibria to other temperatures. The following example illustrates this.

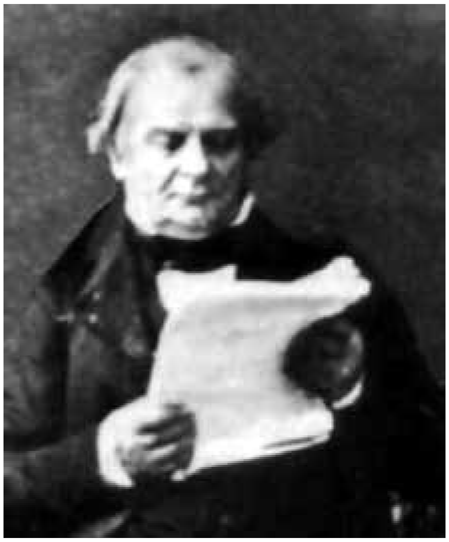

Figure 6.2 Benoit P. E. Clapeyron (1799–1864), French thermodynamicist. Using principles laid down by Carnot, Clapeyron deduced concepts of entropy that eventually led to the second law of thermodynamics.

Example 6.4

Estimate the pressure necessary to melt water at −10°C if the molar volume of liquid water is 18.01 mL and the molar volume of ice is 19.64 mL. $\Delta\overline{S}$ for the process is +22.04 J/K and you can assume that these values remain relatively constant with temperature. You will need this conversion factor: 1 L·bar = 100 J.

Solution

The change in molar volume for the reaction

$$\text{H}_2\text{O (s)} \rightleftharpoons \text{H}_2\text{O } (\ell)$$

is 18.01 mL − 19.64 mL = −1.63 mL. In units of liters, this is -1.63×10^{-3} L. ΔT for this process is −10°C, which is also −10 K. (Recall that *changes* in temperature have the same magnitude in kelvins as they have in degrees Celsius.) $\Delta\overline{S}$ is given, so we use the Clapeyron equation and get

$$\frac{\Delta p}{-10\text{ K}} = \frac{22.04\,\frac{\text{J}}{\text{K}}}{-1.63 \times 10^{-3}\text{ L}}$$

The temperature units cancel to give us, after rearranging,

$$\Delta p = \frac{(-10)(22.04 \text{ J})}{-1.63 \times 10^{-3} \text{ L}}$$

We have to use the given conversion factor to get a recognizable unit of pressure:

$$\Delta p = \frac{(-10)(22.04 \text{ J})}{-1.63 \times 10^{-3} \text{ L}} \times \frac{1 \text{ L·bar}}{100 \text{ J}}$$

The units of J and L cancel, leaving units of bar, which is the standard unit of pressure. Solving:

$$\Delta p = 1.35 \times 10^{3} \text{ bar}$$

Since 1 bar equals 0.987 atm, it takes about 1330 atm to lower the melting point of water to −10°C. This is an estimate, since $\Delta\overline{V}$ and $\Delta\overline{S}$ would be slightly different at −10° than at 0°C (the normal melting point of ice) or at 25°C (the common thermodynamic temperature). However, it is a very good estimate, since both $\Delta\overline{V}$ and $\Delta\overline{S}$ do not vary much over such a small temperature range.

The Clapeyron equation can be applied to substances under extreme conditions of temperature and pressure, since it can estimate the conditions of phase transitions—and therefore the stable phase of a compound—at other than standard conditions. Such conditions might exist, say, at the center of a gas giant planet like Saturn or Jupiter. Or, extreme conditions might be applied in various industrial or synthetic processes. Consider the synthesis of diamonds, which normally occurs deep within the earth (or so it is thought). The phase transition from the stable phase of carbon, graphite, to the "unstable" phase, diamond, is a viable target for the Clapeyron equation, even though the two phases are solids.

Example 6.5

Estimate the pressure necessary to make diamond from graphite at a temperature of 2298 K, that is, with $\Delta T = (2298 - 298)$ K = 2000 K. (This conversion was first achieved industrially by General Electric in 1955.) Use the following information:

	C (s, graphite)	⇌	C (s, diamond)
$\overline{S}$ (J/K)	5.69		2.43
$\overline{V}$ (L)	4.41×10^{-3}		3.41×10^{-3}

Solution

Using the Clapeyron equation, we find that

$$\frac{\Delta p}{2000 \text{ K}} = \frac{(2.43 - 5.69)\frac{\text{J}}{\text{K}}}{(3.41 \times 10^{-3} - 4.41 \times 10^{-3}) \text{ L}} \frac{1 \text{ L·bar}}{100 \text{ J}}$$

where we have included the conversion factor from J to L·bar. Solving for Δp, we get

$$\Delta p = 65{,}200 \text{ bar}$$

as the pressure needed to promote the conversion from graphite to diamond. This is over 65,000 times atmospheric pressure. In reality, much higher pressures, on the order of 100,000 bar, are used to produce synthetic diamonds at these temperatures.

The Clapeyron equation also works for liquid-gas and solid-gas phase transitions, but as we will see shortly, some approximations can be made that allow us to use other equations with minimal error.

Recall that for phase equilibria, $\Delta G = 0$, so that

$$0 = \Delta_{\text{trans}} H - T\,\Delta_{\text{trans}} S$$

This rearranges to

$$\Delta_{\text{trans}} S = \frac{\Delta_{\text{trans}} H}{T}$$

If we assume molar amounts, we can substitute for $\Delta\overline{S}$ in equation 6.9. The Clapeyron equation becomes

$$\frac{dp}{dT} = \frac{\Delta\overline{H}}{T\,\Delta\overline{V}} \tag{6.11}$$

where again we have dropped the "trans" label from $\Delta\overline{H}$. Equation 6.11 is particularly useful because we can bring dT over to the other side of the equation where temperature is a variable:

$$dp = \frac{\Delta\overline{H}}{T\,\Delta\overline{V}}\,dT$$

Rearranging, we get

$$dp = \frac{\Delta\overline{H}}{\Delta\overline{V}}\,\frac{dT}{T}$$

We can now take the definite integral of both sides, one with respect to pressure and one with respect to temperature. Assuming $\Delta\overline{H}$ and $\Delta\overline{V}$ are independent of temperature, we get

$$\int_{p_\text{i}}^{p_\text{f}} dp = \frac{\Delta\overline{H}}{\Delta\overline{V}} \int_{T_\text{i}}^{T_\text{f}} \frac{dT}{T}$$

The integral on the pressure side is the change in pressure, Δp. The integral on the temperature side is the natural logarithm of the temperature, evaluated at the temperature limits. We get

$$\Delta p = \frac{\Delta\overline{H}}{\Delta\overline{V}} \ln \frac{T_\text{f}}{T_\text{i}} \tag{6.12}$$

This expression relates changes in phase-change conditions, but in terms of the molar quantities $\Delta_{\text{trans}}\overline{H}$ and $\Delta_{\text{trans}}\overline{V}$.

Example 6.6

What pressure is necessary to change the boiling point of water from its 1.000-atm value of 100°C (373 K) to 97°C (370 K)? The heat of vaporization of water is 40.7 kJ/mol. The density of liquid water at 100°C is 0.958 g/mL and the density of steam is 0.5983 g/L. You will have to use the relationship 101.32 J = 1 L·atm.

Solution

First, we calculate the change in volume. For 1.00 mole of water that has a mass of 18.01 g, the volume of the liquid is 18.01/0.958 = 18.8 mL. For 1.00 mole of steam, the volume is 18.01/0.5983 = 30.10 L. $\Delta\overline{V}$ is 30.10 L − 18.8 mL = 30.08 L per mole of water. (Notice the units on the volumes.) Using equation 6.12, we find

$$\Delta p = \frac{40{,}700\ \text{J}}{30.08\ \text{L}} \ln \frac{370\ \text{K}}{373\ \text{K}}$$

Notice that we have converted $\Delta\overline{H}$ into units of J. The temperature units cancel; we get

$$\Delta p = 1353\ \text{J/L}\ (-0.00808)$$

$$\Delta p = -10.9\ \text{J/L}$$

At this point, we invoke our conversion factor between J and L·atm:

$$\Delta p = -10.9\ \frac{\text{J}}{\text{L}}\ \frac{1\ \text{L·atm}}{101.32\ \text{J}}$$

The J and L units cancel, leaving units of atm, which are units of pressure:

$$\Delta p = -0.108\ \text{atm}$$

This is the change in pressure from the original pressure of 1.000 atm; the actual pressure at which the boiling point is 97°C is therefore 1.000 − 0.108 atm = 0.892 atm. This would be the pressure about 1000 meters above sea level, or about 3300 feet. Since many people live at that altitude or higher around the world, substantial populations experience water with a boiling point of 97°C.

6.5 The Clausius-Clapeyron Equation

If a gas is involved in the phase transition, we can make a simple approximation. The volume of the gaseous phase is so much larger than the volume of the condensed phase (as Example 6.6 showed) that we introduce only a tiny bit of error if we simply neglect the volume of the condensed phase. We simply use $\overline{V}_{\text{gas}}$ in equation 6.11 and get

$$\frac{dp}{dT} = \frac{\Delta\overline{H}}{T\cdot\overline{V}_{\text{gas}}}$$

If we also assume that the gas obeys the ideal gas law, we can substitute RT/p for the molar volume of the gas:

$$\frac{dp}{dT} = \frac{\Delta\overline{H}\cdot p}{T\cdot RT} = \frac{\Delta\overline{H}\cdot p}{RT^2}$$

Rearranging, we get

$$\frac{dp}{p} = \frac{\Delta\overline{H}}{R}\cdot\frac{dT}{T^2}$$

Recognizing that dp/p is equal to $d(\ln p)$, we have

$$d(\ln p) = \frac{\Delta\overline{H}}{R}\cdot\frac{dT}{T^2} \tag{6.13}$$

which is one form of the *Clausius-Clapeyron equation.* This equation can also be integrated between two sets of conditions, (p_1, T_1) and (p_2, T_2). If we assume constant $\Delta\overline{H}$ over the temperature range, we get

$$\ln \frac{p_1}{p_2} = -\frac{\Delta\overline{H}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{6.14}$$

The Clausius-Clapeyron equation is very useful in considering gas-phase equilibria. For example, it helps predict equilibrium pressures at differing temperatures. Or it can predict what temperature is necessary to generate a particular pressure. Or pressure/temperature data can be used to determine the change in enthalpy for the phase transition.

Example 6.7

All liquids have characteristic *vapor pressures* that vary with temperature. The characteristic vapor pressure for pure water at 22.0°C is 19.827 mmHg and at 30.0°C is 31.824 mmHg. Use these data to calculate the change in enthalpy per mole for the vaporization process.

Solution

We must convert temperatures to kelvins, so those become 295.2 and 303.2 K. Using equation 6.14:

$$\ln \frac{19.827 \text{ mmHg}}{31.824 \text{ mmHg}} = -\frac{\Delta\overline{H}}{8.314\frac{\text{J}}{\text{mol}\cdot\text{K}}}\left(\frac{1}{295.2 \text{ K}} - \frac{1}{303.2 \text{ K}}\right)$$

Evaluating:

$$-0.47317 = -\frac{\Delta\overline{H}}{8.314 \text{ J/mol}}(8.938 \times 10^{-5})$$

$$\Delta\overline{H} = \frac{(0.47317)(8.314)}{(8.938 \times 10^{-5})} \text{ J/mol} = 44{,}010 \text{ J/mol}$$

The heat of vaporization, $\Delta_{\text{vap}}H$, of water is 40.66 kJ/mol at its normal boiling point of 100°C. At 25°C, it is 44.02 kJ/mol—very close to what is predicted by the Clausius-Clapeyron equation. (Note, however, that $\Delta_{\text{vap}}H$ varies by more than 3 kJ/mol over a temperature range of 75°, illustrating that $\Delta_{\text{vap}}H$ does vary with temperature.)

Example 6.8

The vapor pressure of mercury at 536 K is 103 torr. Estimate the normal boiling point of mercury, where the vapor pressure is 760 torr. The heat of vaporization of mercury is 58.7 kJ/mol.

Solution

Using the Clausius-Clapeyron equation, we have

$$\ln \frac{103 \text{ torr}}{760 \text{ torr}} = -\frac{58{,}700 \text{ J}}{8.314 \text{ J/K}}\left(\frac{1}{536 \text{ K}} - \frac{1}{T_{\text{BP}}}\right)$$

where T_{BP} represents the normal boiling point. Rearranging and canceling the appropriate units, we get

$$0.000283 \text{ K}^{-1} = 0.00187 \text{ K}^{-1} - \frac{1}{T_{\text{BP}}}$$

Solving for the boiling point:

$$T_{\mathrm{BP}} = 632 \text{ K}$$

The measured boiling point of mercury is 629 K.

The previous example illustrates how well the Clausius-Clapeyron equation works, despite the assumptions used in deriving it. It also shows that the vapor pressure of a substance is related by its *logarithm* to the absolute temperature. That is,

$$\ln(\text{vapor pressure}) \propto T \tag{6.15}$$

Another way of stating this is by taking the inverse logarithm of both sides to get

$$\text{vapor pressure} \propto e^{T} \tag{6.16}$$

As the temperature increases, the vapor pressure increases faster and faster, and many plots of vapor pressure versus temperature have an exponential look to them. Equations 6.15 and 6.16 do not conflict with the ideal gas law (in which p is directly proportional to T) because these two equations apply to phase equilibria and are not meant to be taken as equations of state for the vapor phase.

6.6 Phase Diagrams and the Phase Rule

Although phase transitions can seem complicated, there is a simplification: the phase diagram. *Phase diagrams* are graphical representations of what phases are stable under various conditions of temperature, pressure, and volume. Most simple phase diagrams are two-dimensional, with pressure on one axis and temperature on the other.

The phase diagram itself is composed of lines that indicate the temperature and pressure values at which phase equilibrium occur. For example, Figure 6.3 is a partial phase diagram of H_2O. The diagram shows the stable phase in each region of the diagram. The lines on the phase diagram represent the phase transitions. Any point on a line represents a particular pressure and temperature at which multiple phases can exist in equilibrium. Any point not on a line indicates a phase that is the predominant stable phase of the compound H_2O under those conditions.

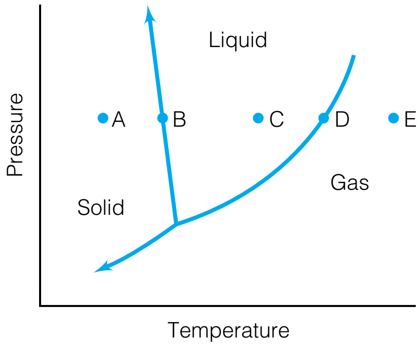

Figure 6.3 A qualitative, partial phase diagram (pressure versus temperature) of H_2O. Specific points in a phase diagram (like points A, B, C, D, and E here) indicate conditions of pressure and temperature and what phase(s) of the component are stable under those conditions.

Consider the points labeled in Figure 6.3. Point A represents a value for pressure p_A and temperature T_A in which the solid form of H_2O is stable. Point B represents a set of pressure and temperature conditions p_B and T_B where melting occurs: solid can exist in equilibrium with liquid. Point C represents pressure and temperature conditions in which liquid is the stable phase. Point D represents pressure and temperature conditions in which liquid can exist in equilibrium with the gas: boiling occurs. Finally, point E represents a set of pressure and temperature conditions in which the stable phase of H_2O is gaseous.

The phase diagram implies that under many conditions solid and liquid can exist in equilibrium, and under many conditions liquid and gas can exist in equilibrium. This is certainly the case. But what are these lines giving us? Since they are a plot of how the pressure changes with change in temperature for the phase equilibria, the lines represent dp/dT. This quantity can be calculated using the Clapeyron or the Clausius-Clapeyron equations. *Single-component phase diagrams are nothing more than plots of the Clapeyron equation or the Clausius-Clapeyron equation for a substance.* This is true for pressure-temperature phase diagrams, which is what we will consider almost exclusively here. For a phase diagram where volume as well as pressure and temperature varies, a three-dimensional plot would be necessary and the equation of state for all phases would be needed.

Example 6.9

The line between the solid and liquid phases for the H_2O phase diagram in Figure 6.3 is a fairly straight line, indicating a constant slope. Use the answers to Example 6.4, the melting of ice, to calculate the value for the slope of that line.

Solution

Recall that one definition of the slope of a line is $\Delta y/\Delta x$. The y-axis represents pressure and the x-axis represents temperature, so for $\Delta p/\Delta T$ we expect a slope where the units are bar/K or atm/K. Example 6.4 showed that it takes 1.35×10^3 bar to change the melting point of water by $-10°\text{C}$, which is -10 K. Therefore, $\Delta p/\Delta T$ is equal to $(1.35 \times 10^3 \text{ bar})/(-10 \text{ K})$ or -1.35×10^2 bar/K. This is a fairly large slope.

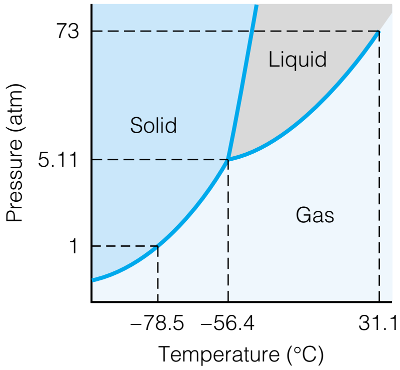

Figure 6.4 A phase diagram for carbon dioxide, CO_2. Notice that as the temperature of solid CO_2 is increased at standard pressure, the solid goes directly into the gas phase. Liquid CO_2 is stable only at increased pressure.

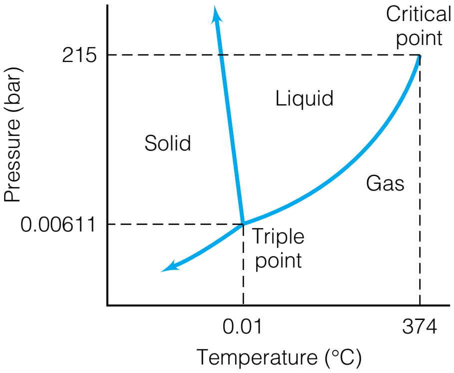

Figure 6.5 The triple point and the critical point for H_2O. The liquid-gas equilibrium line is the only one that ends at a certain set of conditions for all substances. For H_2O, the line ends at 374°C and 215 bar. At higher temperatures or vapor pressures, there is no distinction between a "liquid" and a "gas" phase.

One other thing to notice from the example is that the slope is negative. Almost all compounds have a positive slope for the solid-liquid equilibrium line, because solids have less volume than the same amount of liquid. The negative slope is a consequence of the *increase* in volume experienced by H_2O when it solidifies.

The solid-gas equilibrium line represents those conditions of pressure and temperature where sublimation occurs. For H_2O, obvious sublimation occurs at pressures lower than those that are normally experienced. (Sublimation of ice does occur slowly at normal pressures, which is why ice cubes get smaller over time in your freezer. The so-called freezer burn of frozen foods is caused by sublimation of ice from the food. This is why it's important to wrap frozen food tightly.) However, for carbon dioxide, normal pressures are low enough for sublimation. Figure 6.4 shows a phase diagram for CO_2, with the 1-atm position marked. Liquid CO_2 is stable only under pressure. Some gas cylinders of carbon dioxide are high enough in pressure that they actually contain liquid CO_2.

The liquid-gas equilibrium line represents conditions of pressure and temperature where those phases can exist at equilibrium. Notice that it has the form of an exponential equation; that is, $p \propto e^T$. This is consistent with equation 6.16. The vaporization line in the phase diagram is a plot of the Clapeyron equation or the Clausius-Clapeyron equation. Notice, however, that this line ends at a particular pressure and temperature, as shown in Figure 6.5. It is the only line that doesn't have an arrow on its end to indicate that it continues. That's because beyond a certain point, the liquid phase and the gas phase become indistinguishable. This point is called the *critical point* of the substance. The pressure and temperature at that point are called the *critical pressure* p_C and *critical temperature* T_C. For H_2O, p_C and T_C are 218 atm and 374°C. Above that temperature, no pressure can force the H_2O molecules into a definite liquid state. If the H_2O in the system exerts a pressure higher than p_C, then it cannot

Table 6.3 Critical temperatures and pressures for various substances

Substance	T_C (K)	p_C (bar)
Ammonia	405.7	111
Hydrogen	32.98	12.93
Methane	191.1	45.2
Nitrogen	126	33.1
Oxygen	154.6	50.43
Sulfur	1314	207
Water	647.3	215.15

exist as a definite liquid or gas. (It can exist as a solid if the temperature is low enough.) The state of the H_2O is called *supercritical.* Supercritical phases are important in some industrial and scientific processes. In particular, there is a technique called supercritical fluid chromatography in which compounds are separated using supercritical CO_2 or other compounds as a "solvent." (T_C and p_C for CO_2 are about 304 K and 73 bar.)*

One other point in the phase diagram is worthy of mention. Figure 6.5 indicates a set of conditions where solid, liquid, and gas are in equilibrium with each other. This is called the *triple point.* For H_2O, the triple point is 0.01°C, or 273.16 K, and 6.11 mbar, or about 4.6 torr. Because H_2O is so common, the triple point for H_2O is recognized internationally as a verifiable temperature standard. All materials have triple points, a unique set of pressure and temperature conditions in which all three phases can exist in equilibrium with each other. Table 6.3 lists conditions of critical points for some substances.

The phase diagram for H_2O is commonly used as an example for several reasons: it is a common material, and the phase diagram shows some unusual characteristics. Figure 6.6 shows a more expansive phase diagram for the

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*One method of decaffeinating coffee beans is by using supercritical CO_2.

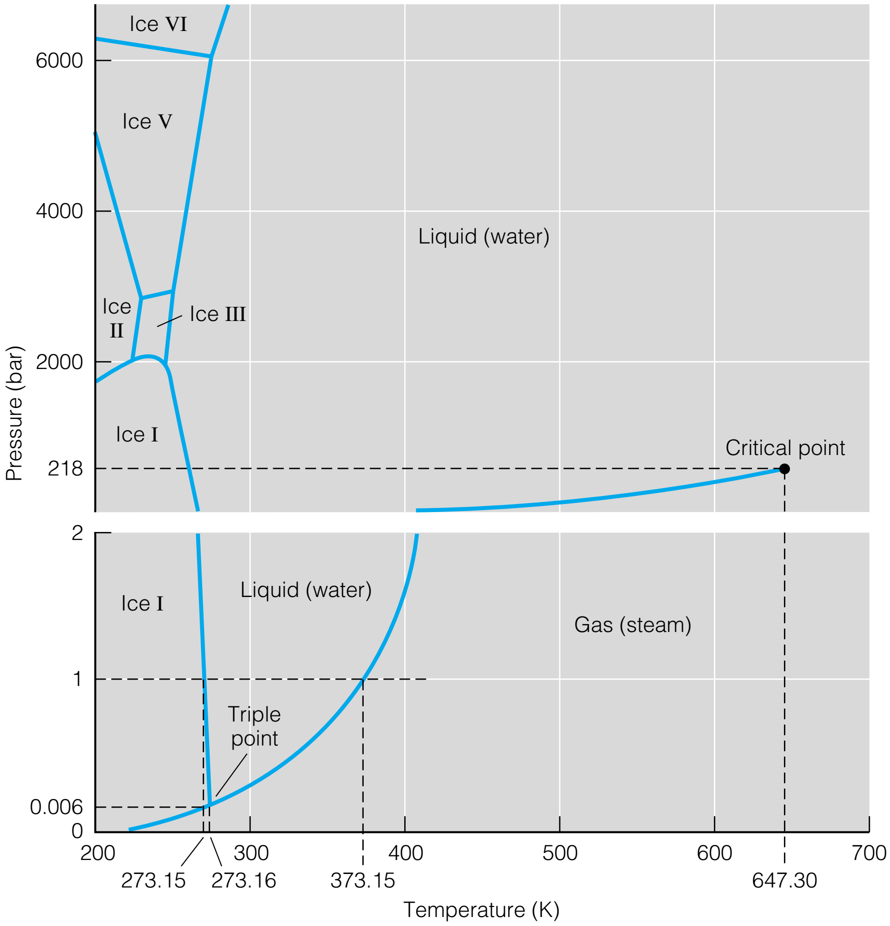

Figure 6.6 This phase diagram of water extends to higher temperatures and pressures than Figure 6.3. Notice that there are several possible crystal structures of solid H_2O, most of which exist only at high pressures. Two forms of solid H_2O have only recently been discovered.

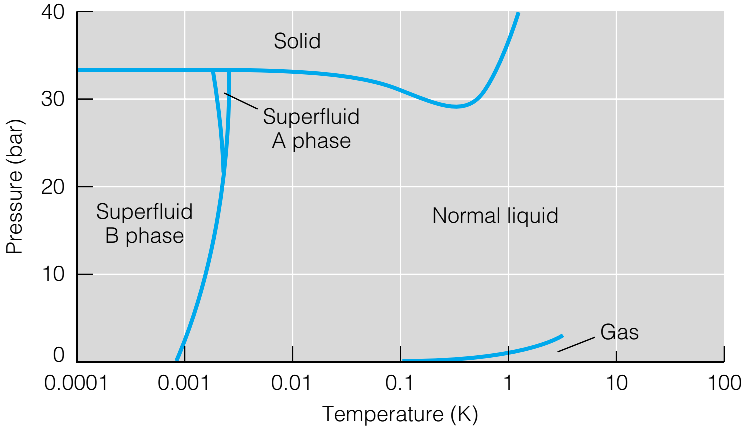

Figure 6.7 The phase diagram of helium, He, does not need a large temperature range. Notice that solid He does not exist unless pressures are large.

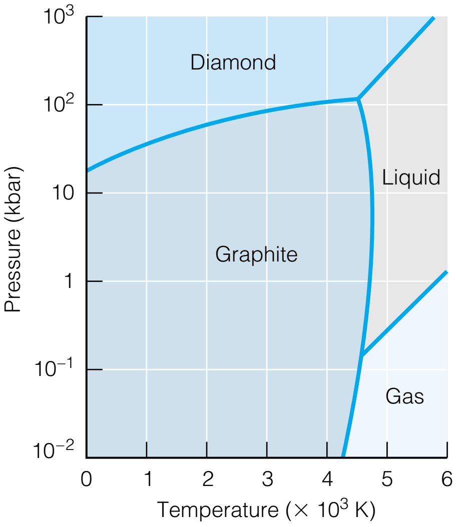

Figure 6.8 A phase diagram of carbon, showing where the graphite allotrope is stable and where the diamond allotrope is stable.

compound H_2O. One of the noteworthy points is that there are actually several types of solid H_2O, that is, ice. Note the pressure and temperature scales, however. We are not likely to experience these forms of ice outside the laboratory.

Figure 6.7 shows a phase diagram of helium. Because helium is a gas at temperatures down to 4.2 K, the temperature axis on this diagram does not have a large temperature range. At the other extreme, Figure 6.8 shows a phase diagram of carbon. Notice the regions where diamond is the stable phase.

Although pressure and temperature are the common variables for phase diagrams in chemistry, volume can also be plotted on an axis in a phase diagram, as shown in Figure 6.9. There are also three-dimensional phase diagrams that plot pressure, volume, and temperature; Figure 6.10 shows an example of that.

Phase diagrams are very useful in helping to understand how single-component systems act under a change in condition: simply plot the change on

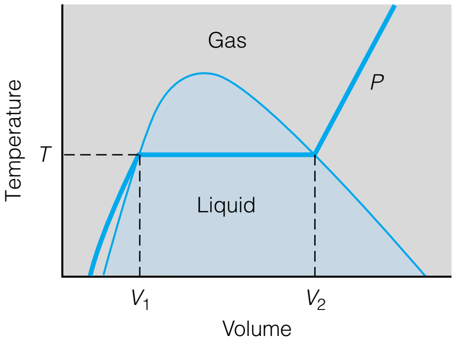

Figure 6.9 An example of a temperature-volume phase diagram. At a certain pressure P, the phase diagram specifies what phase must be present except between V_1 and V_2 (for the given pressure). Under these conditions, a varying amount of liquid phase (shaded area) may be present and still satisfy the given conditions of T and P. In part because of this ambiguity, temperature-volume phase diagrams aren't as common as pressure-temperature phase diagrams.

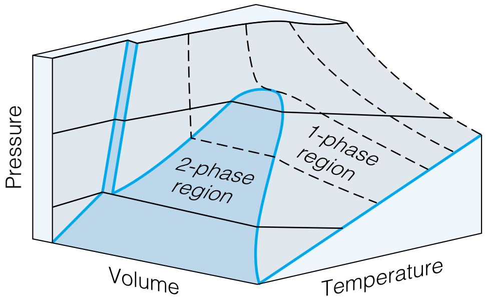

Figure 6.10 A three-dimensional phase diagram can plot the phases present in a system for given sets of pressures, temperatures, and volumes.

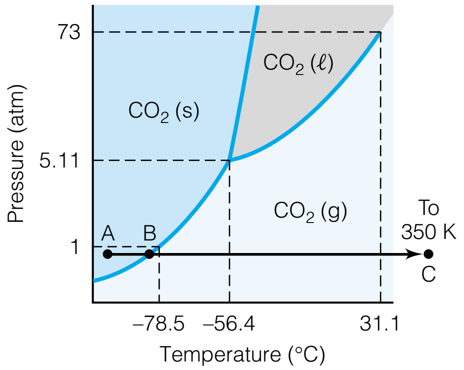

Figure 6.11 An illustration of the isobaric change for CO_2 specified in Example 6.10a. Compare this to Figure 6.12.

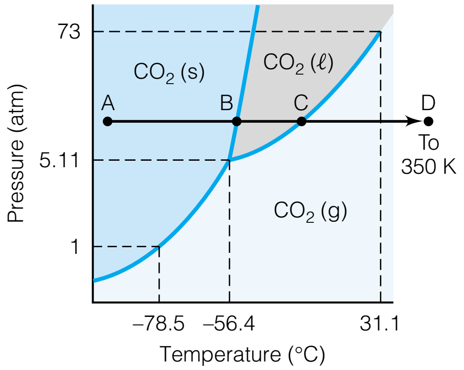

Figure 6.12 An illustration of the isobaric change for CO_2 specified in Example 6.10b. Compare this to Figure 6.11.

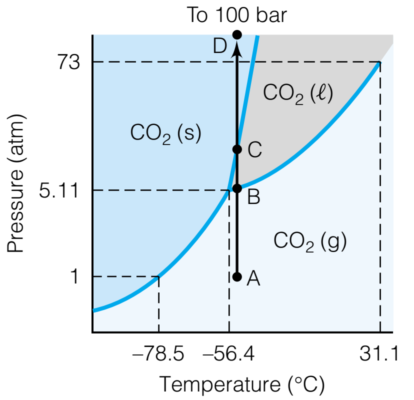

Figure 6.13 An illustration of the change specified in Example 6.10c.

the phase diagram and observe which phase transitions occur for that change. Single-component phase diagrams are especially easy to interpret.

Example 6.10

Use the phase diagram of CO_2, Figure 6.4, to describe the changes in phase as one makes the following changes in conditions.

a. 50 K to 350 K at a pressure of 1.00 bar
b. 50 K to 350 K at a pressure of 10 bar
c. 1 bar to 100 bar at a temperature of 220 K

Solution

a. Figure 6.11 shows the change in conditions for this isobaric process. Starting at point A, the temperature is increased as we move from left to right, indicating that we are warming the solid CO_2, until we reach the line at point B indicating the equilibrium between solid and gas phases. At this point, the solid CO_2 sublimes directly into the gas phase. (This occurs at about 196 K, or −77°C.) As the temperature increases to 350 K, we are warming gaseous CO_2 until we reach point C, the final conditions.

b. Figure 6.12 shows the change in conditions for the isobaric warming of CO_2 at 10 bar. In this case, we start with a solid at point A, but since we are above the critical point for CO_2, at point B we are in an equilibrium with solid and liquid CO_2 present. As we add heat, solid melts until all solid becomes liquid, and then the liquid CO_2 warms. We continue warming until point C is reached, which represents the conditions where CO_2 liquid is in equilibrium with CO_2 gas. When all of the liquid is converted to gas, the gas warms until the final conditions at point D are reached.

c. Figure 6.13 illustrates the isothermal process. The starting point A is at low enough pressure that the CO_2 is in the gas phase. However, as the pressure is increased, the CO_2 passes into the liquid phase (briefly) and then into the solid phase. Note that if the temperature were only a few degrees lower, this change would have occurred on the other side of the triple point and the phase transition would have been a direct gas-to-solid condensation.

Phase diagrams of single-component systems are useful in illustrating a simple idea that answers a common question: How many variables must be specified in order to determine the phase(s) of the system when it's at equilibrium? These variables are called *degrees of freedom*. What we need to know is how many degrees of freedom we need to specify in order to characterize the state of the system. This information is more useful than one might think. Because the position of phase transitions (especially transitions that involve the gas phase) can change quickly with pressure or temperature, knowing how many state variables *must* be defined is important.

Consider the two-dimensional phase diagram for H_2O. If you knew that only H_2O was in the system at equilibrium and that it was in the solid phase, then any point in the shaded region of Figure 6.14 would be possible. You would have to specify both the temperature and the pressure of the system. However, suppose you knew that you had solid *and* liquid H_2O in the system at equilibrium. Then you know that the condition of the system must be indicated by the line in the phase diagram that separates the solid and liquid phase. You need only specify temperature *or* pressure, because knowing one gives you the other (because the system—with two phases in

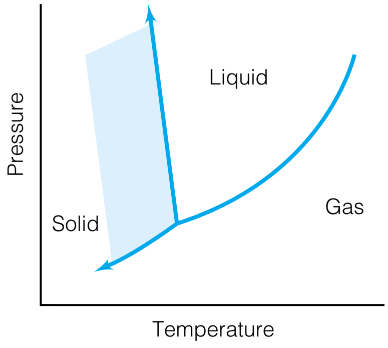

Figure 6.14 If all you know about a system is that H_2O is solid, then any set of pressure and temperature conditions in the shaded area would be possible conditions of the system. You will need to specify two degrees of freedom to describe your system.

equilibrium—must have conditions corresponding to that line). The number of degrees of freedom has dropped because the number of phases in your system has increased.

Suppose you know that you have three phases of H_2O in your system at equilibrium. You don't have to specify any degrees of freedom because there is *only one* set of conditions in which that will occur: for H_2O, those conditions are 273.16 K and 6.11 mbar. (See Figure 6.5: there is only one point on that phase diagram where solid, liquid, and gas exist in equilibrium, and that is the triple point.) There is a relationship between the number of phases occurring at equilibrium and the number of degrees of freedom necessary to specify the point in the phase diagram that describes the state of the system.

In the 1870s, J. Willard Gibbs (for whom Gibbs free energy is named) deduced the simple relationship between the number of degrees of freedom and the number of phases. For a single-component system,

$$\text{degrees of freedom} = 3 - P \tag{6.17}$$

where P represents the number of phases present at equilibrium. Equation 6.17 is a simplified version of what is known as the *Gibbs phase rule.* In this rendition, it assumes that one of the state variables of the system, usually the volume, can be determined from the others (via an equation of state). You should verify that this simple equation provides the correct number of degrees of freedom for each situation described above.

6.7 Natural Variables and Chemical Potential

We have implied previously that the conditions of the phase equilibrium depend on the state variables of the system, namely volume, temperature, pressure, and amount. Usually we deal with changes in systems as temperature and pressure vary. It would therefore be useful to know how the chemical potential varies with respect to temperature and pressure. That is, we want to know $(\partial\mu/\partial T)$ and $(\partial\mu/\partial p)$. The chemical potential is the change in the Gibbs free energy with respect to amount. For a pure substance, the total Gibbs free energy of a system is

$$G = \mu \cdot n$$

where n is the number of moles of the material having chemical potential μ. [This expression comes directly from the definition of μ, which is $(\partial G/\partial n)_{T,p}$.] From the relationship between G and μ presented in Chapter 4, and knowing how G itself varies with T and p (given in equations 4.24 and 4.25), we can get

$$\left(\frac{\partial\mu}{\partial T}\right)_{p,n} = -\overline{S} \tag{6.18}$$

and

$$\left(\frac{\partial\mu}{\partial p}\right)_{T,n} = \overline{V} \tag{6.19}$$

The natural variable equation for $d\mu$ is

$$d\mu = -\overline{S}\,dT + \overline{V}\,dp \tag{6.20}$$

This is similar to the natural variable equation for G. We can also write the derivatives from equations 6.18 and 6.19 in terms of the *change* in chemical potential, $\Delta\mu$. This will be more relevant when we consider phase transitions. Equations 6.18 and 6.19 can be rewritten as

$$\left[\frac{\partial(\Delta\mu)}{\partial T}\right]_p = -\Delta\overline{S} \tag{6.21}$$

$$\left[\frac{\partial(\Delta\mu)}{\partial p}\right]_T = \Delta\overline{V} \tag{6.22}$$

We can use these equations to predict what direction an equilibrium will move if conditions of T or p are changed. Consider the solid-to-liquid phase transition. Liquids typically have greater entropy than solids, so going from solid to liquid is an *increase* in entropy, and the negative sign on the right of equation 6.21 implies that the slope of the μ versus T plot is negative. Thus, as temperature increases, the chemical potential *decreases.* Since chemical potential is defined in terms of an energy—here, the Gibbs free energy—and since spontaneous changes have negative changes in the Gibbs free energies, as the temperature increases the system will tend toward the phase with the *lower* chemical potential: the liquid. Equation 6.21 explains why substances melt when the temperature is increased.

The same argument applies for the liquid-to-gas phase transition. In this case, the slope of the curve is usually higher because the difference in entropy between liquid and gas phases is much larger in magnitude than the difference in S between solid and liquid phases. However, the reasoning is the same, and equation 6.21 explains why liquids change to gas when the temperature is increased.

The effects of pressure on the equilibrium depend on the molar volumes of the phases. Again, the magnitude of the effect depends on the relative change in the molar volume. Between solid and liquid, volume changes are usually very small. That is why pressure changes do not substantially affect the position of solid-liquid equilibria, unless the change in pressure is very large. However, for liquid-gas (and solid-gas, for sublimation) transitions, the change in molar volume can be on the order of hundreds or thousands of times. Pressure changes have substantial effects on the relative positions of phase equilibria involving the gas phase.

Equation 6.22 is consistent with the behavior of the solid and liquid phases of water. Water is one of the few substances whose solid molar volume is larger than its liquid molar volume.* Equation 6.22 implies that an increase in pressure (Δp is positive) would drive a phase equilibrium toward the phase that has the *lower* molar volume (since for spontaneous changes, the Gibbs free energy goes down). For most substances, an increase in pressure would drive the equilibrium towards the solid phase. But water is one of the few chemical substances (elemental bismuth is another) whose liquid is denser than its solid. Its $\Delta\overline{V}$ term for equation 6.22 is positive when going from liquid to solid, so for a spontaneous process (that is, $\Delta\mu$ negative), an increase in pressure translates into going from solid to liquid. This is certainly unusual behavior—but it is consistent with thermodynamics.

Example 6.11

In terms of the variables in equations 6.21 and 6.22, state what happens to the following equilibria when the given changes in conditions are imposed. Assume all other conditions are kept constant.

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*Another way to say this is that a given amount of liquid is denser than the same amount of solid.

a. Pressure is increased on the equilibrium H_2O (s, $\overline{V}$ = 19.64 mL) $\rightleftharpoons$ H_2O (ℓ, $\overline{V}$ = 18.01 mL).

b. Temperature is decreased on the equilibrium glycerol (ℓ) $\rightleftharpoons$ glycerol (s).

c. Pressure is decreased on the equilibrium $CaCO_3$ (aragonite, $\overline{V}$ = 34.16 mL) $\rightleftharpoons$ $CaCO_3$ (calcite, $\overline{V}$ = 36.93 mL).

d. Temperature is increased on the equilibrium CO_2 (s) $\rightleftharpoons$ CO_2 (g).

Solution

a. The change in molar volume for the reaction as written is −1.63 mL. Since Δp is positive and a spontaneous process is accompanied by a negative $\Delta\mu$, the expression $\Delta\mu/\Delta p$ will be negative overall. Therefore, the equilibrium will move in the direction of the negative $\Delta\overline{V}$, so the equilibrium will go toward the liquid phase.

b. Since ΔT is negative and a spontaneous process is accompanied by a negative $\Delta\mu$, the expression $\Delta\mu/\Delta T$ will be positive. Therefore, the reaction will proceed in the direction that provides a negative $\Delta\overline{S}$ (as a consequence of the negative sign in equation 6.21). The equilibrium will move in the direction of the solid glycerol.

c. Δp is negative, so the reaction will spontaneously move in the direction of the positive change in volume. The equilibrium will move toward the calcite phase.

d. ΔT is positive, and $\Delta\mu$ for a spontaneous transition must be negative, so the equilibrium moves in the direction of increased entropy: toward the gas phase.

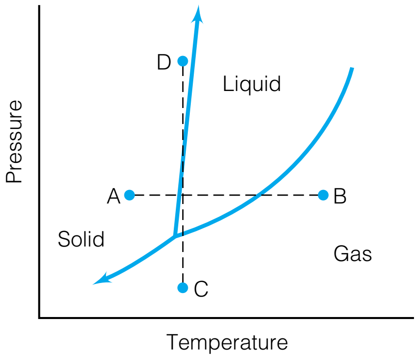


Figure 6.15 The lines A → B and C → D reflect changes in conditions, and the phase transitions along each line are related to the differences in the chemical potentials of the component, as given by equations 6.21 and 6.22. See the text for details.

Let us interpret these expressions in terms of phase diagrams and the phase transitions that they represent. First, we recognize the general magnitudes of the entropy of the various phases as $\overline{S}_{\text{solid}} < \overline{S}_{\text{liquid}} < \overline{S}_{\text{gas}}$. We also recognize the general magnitude of the volumes of the various phases as $\overline{V}_{\text{solid}} < \overline{V}_{\text{liquid}} < \overline{V}_{\text{gas}}$. (However, see our discussion of water below.)

In considering the change in chemical potential as temperature changes but at constant pressure (equation 6.21), we are moving across the horizontal line in Figure 6.15, from point A to point B. The derivative in equation 6.21, which describes this line, suggests that as T increases, the chemical potential must decrease so that the entropy change, $\Delta\overline{S}$, is negative. For a phase transition that involves solid to liquid (melting), solid to gas (sublimation), or liquid to gas (boiling), the entropy *always* increases. Therefore, the negative of $\Delta\overline{S}$ for these processes will *always* have a negative value. In order to satisfy equation 6.21, phase transitions accompanying an increase in temperature must always occur with a simultaneous decrease in the chemical potential. Since chemical potential is ultimately an energy—it was originally defined in terms of the Gibbs free energy—what we are saying is that the system will tend toward a state of minimum energy. This is consistent with the idea from the last chapter that systems tend toward the state of minimum (free) energy. We have two different statements pointing to the same conclusion, so there is self-consistency in thermodynamics. (All good theories must be self-consistent in such situations.)

But the basic statement, one that agrees with common experience, is simple. At low temperatures, substances are solids; as you heat them, they melt into liquids; as you heat them more, they become gases. Such common experiences are consistent with the equations of thermodynamics. [You should recognize by now that the existence of the liquid phase depends on the pressure. If the pressure of the system is lower than the critical pressure, the solid will sublime (as CO_2 commonly does). If the temperature is higher than the critical temperature, then the solid will "melt" into a supercritical fluid. The A → B line in Figure 6.15 was intentionally selected to sample all three phases.]

Equation 6.22 is related to the vertical line in Figure 6.15 that connects points C and D. As the pressure is increased at constant temperature, the chemical potential also increases because for (almost) all substances, the relation $\overline{V}_{\text{solid}} < \overline{V}_{\text{liquid}} < \overline{V}_{\text{gas}}$ applies. That is, the volume of the solid is smaller than the volume of the liquid, which is in turn smaller than the volume of the gas. Therefore, as one increases the pressure, one tends to go to the phase that has the smaller volume: this is the only way for the partial derivative in equation 6.22 to remain negative. If systems tend to go to lower chemical potential, then the numerator $\partial(\Delta\mu)$ is negative. But if ∂p is positive—the pressure is increased—then the overall fraction on the left side of equation 6.22 represents a negative number. Therefore, systems tend to go to phases that have smaller volumes when the pressure is increased. Since solids have lower volumes than liquids, which have smaller volumes than gases, increasing the pressure at constant temperature takes a component from gas to liquid to solid: exactly what is experienced.

Except for H_2O. Because of the crystal structure of solid H_2O, the solid phase of H_2O has a larger volume than the equivalent amount of liquid-phase H_2O. This is reflected in the negative slope of the solid-liquid equilibrium line in the phase diagram of H_2O, Figure 6.3. When the pressure is increased (at certain temperatures), the liquid phase is the stable phase, not the solid phase. H_2O is the exception, not the rule. It's just that water is so common, and its behavior so accepted by us, that we tend to forget the thermodynamic implications.

There is also a Maxwell relationship that can be derived from the natural variable equation for chemical potential μ. It is

$$\left(\frac{\partial \overline{S}}{\partial p}\right)_T = -\left(\frac{\partial \overline{V}}{\partial T}\right)_p \tag{6.23}$$

However, since this is the same relation as equation 4.37 from the natural variable equation for G, it does not provide any new, usable relationships.

6.8 Summary

Single-component systems are useful for illustrating some of the concepts of equilibrium. Using the concept that the chemical potential of two phases of the same component must be the same if they are to be in equilibrium in the same system, we were able to use thermodynamics to determine first the Clapeyron and then the Clausius-Clapeyron equation. Plots of the pressure and temperature conditions for phase equilibria are the most common form of phase diagram. We use the Gibbs phase rule to determine how many conditions we need to know in order to specify the exact state of our system.

For systems with more than one chemical component, there are additional considerations. Solutions, mixtures, and other multicomponent systems can be described using some of the tools described in this chapter, but because of the presence of multiple components, more information is necessary to describe the exact state. We will consider some of those tools in the next chapter.

EXERCISES FOR CHAPTER 6

6.2 Single-Component Systems

6.1. Determine the number of components in the following systems: **(a)** an iceberg of pure H_2O; **(b)** bronze, an alloy of copper and tin; **(c)** Wood's metal, an alloy of bismuth, lead, tin, and cadmium (it is used in sprinkler systems for fire control); **(d)** vodka, a mixture of water and ethyl alcohol; **(e)** a mixture of sand and sugar.

6.2. Coffee is an extract of a roasted bean, made with hot water. It has many components. Some companies market instant coffee, which is made by freeze-drying brewed coffee. Explain from a components perspective why instant coffee rarely has the quality of freshly brewed coffee.

6.3. How many different single-component systems can be made from metallic iron and chlorine gas? Assume that the components are chemically stable.

6.4. Explain how solid and liquid phases of a substance can exist in the same closed, adiabatic system at equilibrium. Under what conditions can solid and gas phases exist at equilibrium?

6.5. Liquid water at room temperature is placed in a syringe, which is then sealed. The plunger of the syringe is drawn back, and at some point bubbles of H_2O vapor are formed. Explain why we can state that the water is boiling.

6.6. If a system is not adiabatic, then heat leaves or enters the system. What is the immediate response of a system **(a)** in liquid-gas equilibrium if heat is removed? **(b)** in solid-gas equilibrium if heat is added? **(c)** in liquid-solid equilibrium if heat is removed? **(d)** composed entirely of solid phase if heat is removed?

6.7. How many values of the normal boiling point does any pure substance have? Explain your answer.

6.8. Write equation 6.2 in a different, yet algebraically equivalent way. Explain why this is an equivalent expression.

6.3 Phase Transitions

6.9. Identify and explain the sign on $\Delta_{\text{trans}}H$ in equation 6.5 if it is used for **(a)** a solid-to-gas phase transition (sublimation), **(b)** a gas-to-liquid phase transition (condensation).

6.10. Calculate the amount of heat necessary to change 100.0 g of ice at $-15.0°\text{C}$ to steam at 110°C. You will need the values of the heat capacity for ice, water, and steam, and $\Delta_{\text{fus}}H$ and $\Delta_{\text{vap}}H$ for H_2O from Tables 2.1 and 2.3. Is this process exothermic or endothermic?

6.11. Citrus farmers sometimes spray water on the fruit trees when a frost is expected. Use equations 6.4 to explain why.

6.12. What is the numerical change in chemical potential of 1 mole of carbon dioxide, CO_2, as it changes temperature? Assume that we are considering the infinitesimal change in chemical potential as the temperature changes infinitesimally starting at 25°C. *Hint:* See equation 4.40.

6.13. What is ΔS for the isothermal conversion of liquid benzene, C_6H_6, to gaseous benzene at its boiling point of 80.1°C? Is it consistent with Trouton's rule?

6.14. Estimate the melting point of nickel, Ni, if its $\Delta_{\text{fus}}H$ is 17.61 kJ/mol and its $\Delta_{\text{fus}}S$ is 10.21 J/mol·K. (Compare this to a measured melting point of 1455°C.)

6.15. Estimate the boiling point of platinum, Pt, if its $\Delta_{\text{vap}}H$ is 510.4 kJ/mol and its $\Delta_{\text{vap}}S = 124.7$ J/mol·K. (Compare this to a measured melting point of 3827 ±100°C.)

6.16. In ice skating, the blade of the skate is thought to exert enough pressure to melt ice, so that the skater glides smoothly on a thin film of water. What thermodynamic principle is involved here? Can you perform a rough calculation to determine whether this is indeed the active mechanism in ice skating? Would skating work if it were performed on other solids and this were the mechanism involved?

6.4 & 6.5 The Clapeyron and Clausius-Clapeyron Equations

6.17. The integration of equation 6.11 to get 6.12 uses what assumption?

6.18. Does the expression $d\mu_{\text{phase1}} = d\mu_{\text{phase2}}$ in the derivation of the Clapeyron equation imply that only a closed system is being considered? Why or why not?

6.19. Sulfur, in its cyclic molecular form having the formula S_8, is an unusual element in that the solid form has two easily accessible solid phases. The rhombic crystal solid is stable at temperatures lower than 95.5°C, and has a density of 2.07 g/cm^3. The monoclinic phase, stable at temperatures higher than 95.5°C and less than the melting point of sulfur, has a density of 1.96 g/cm^3. Use equation 6.10 to estimate the pressure necessary to make rhombic sulfur the stable phase at 100°C if the entropy of transition is 1.00 J/mol·K. Assume that $\Delta_{\text{trans}}S$ does not change with changing conditions.

6.20. Refer to exercise 6.19. How applicable is $\Delta_{\text{trans}}S$ at *standard* pressure to the extreme condition of pressure necessary for the stated phase transition? How accurate do you think your answer to exercise 6.19 is?

6.21. State whether or not the Clausius-Clapeyron equation is strictly applicable to the following phase transitions.

(a) Sublimation of ice in your freezer

(b) Condensation of steam into water

(c) Freezing of cyclohexane at 6.5°C

(d) Conversion of ice VI to ice VII (see Figure 6.6)

(e) Conversion of diatomic oxygen, O_2 (g), to triatomic ozone, O_3 (g)

(f) Formation of diamonds under pressure

(g) Formation of metallic solid hydrogen, H_2, from liquid hydrogen. (The transformation to metallic hydrogen occurs under megabars of pressure and may be part of gas giant planets like Jupiter and Saturn.)

(h) Evaporation of mercury liquid, Hg (ℓ), from a broken thermometer.

6.22. In words, explain what slope the Clapeyron equation can calculate. That is, a plot of what measurement with respect to what other measurement can be *calculated* by equation 6.9?

6.23. Consider the sulfur solid-state phase transition in exercise 6.19. Given that $\Delta_{\text{trans}}H$ for the rhombic-to-monoclinic phase transition is 0.368 kJ/mol, use equation 6.12 to estimate the pressure necessary to make the rhombic phase stable at 100°C. Additional necessary data is given in exercise 6.19. How does this pressure compare to the answer in 6.19?

6.24. If it takes 1.334 megabars of pressure to change the melting point of a substance from 222°C to 122°C for a change in molar volume of -3.22 cm^3/mol, what is the heat of fusion of the substance?

6.25. Reusable hot-packs sometimes use the precipitation of supersaturated sodium acetate or calcium acetate to give off heat of crystallization to warm a person. Can the conditions of this phase transition be understood in terms of the Clapeyron or the Clausius-Clapeyron equation? Why or why not?

6.26. Four alcohols have the formula C_4H_9OH: 1-butanol, 2-butanol (or *sec*-butanol), isobutanol (or 2-methyl-1-propanol), and *tert*-butanol (or 2-methyl-2-propanol). They are examples of *isomers,* or compounds that have the same molecular formula but different molecular structures. The following table gives data on the isomers:

Compound	$\Delta_{\text{vap}}H$ (kJ/mol)	Normal boiling point (°C)
1-Butanol	45.90	117.2
2-Butanol	44.82	99.5
Isobutanol	45.76	108.1
tert-Butanol	43.57	82.3

Using the Clausius-Clapeyron equation, rank the isomers of butanol in order of decreasing vapor pressure at 25°C. Does the ranking agree with any conventional wisdom based on the $\Delta_{\text{vap}}H$ values or the normal boiling points?

6.27. What is the rate of change of pressure as temperature changes (that is, what is dp/dT) for the vapor pressure of naphthalene, $C_{10}H_8$, used in mothballs, at 22.0°C if the vapor pressure at that temperature is 7.9×10^{-5} bar and the heat of vaporization is 71.40 kJ/mol? Assume that the ideal gas law holds for the naphthalene vapor at that temperature and pressure.

6.28. Using the data in the previous problem, determine the vapor pressure of naphthalene at 100°C.

6.29. In high-temperature studies, many compounds are vaporized from crucibles that are heated to a high temperature. (Such materials are labeled *refractory*.) The vapors stream out of a small hole into an experimental apparatus. Such a crucible is called a *Knudsen cell.* If the temperature is increased linearly, what is the relationship to the change in the pressure of the vaporized compound? Can you explain why it is important to be careful when vaporizing materials at high temperatures?

6.30. At what pressure does the boiling point of water become 300°C? If oceanic pressure increases by 1 atm for every 10 m (33 ft), what ocean depth does this pressure correspond to? Do ocean depths that deep exist on this planet? What is the potential implication for underwater volcanoes?

6.31. For liquid droplets, the unequal interactions of the liquid molecules with other liquid molecules at a surface give rise to a *surface tension,* γ. This surface tension becomes a component of the total Gibbs free energy of the sample. For a single-component system, the infinitesimal change in G can be written as

$$dG = -S\,dT + V\,dp + \mu_{\text{phase}}\,dn_{\text{phase}} + \gamma\,dA$$

where dA represents the change in surface area of the droplet. At constant pressure and temperature, this equation becomes

$$dG = \mu_{\text{phase}}\,dn_{\text{phase}} + \gamma\,dA$$

For a spherical droplet having radius r, the area A and volume V are $4\pi r^2$ and $\frac{4}{3}\pi r^3$, respectively. It can therefore be shown that

$$dA = \frac{2\,dV}{r} \tag{6.24}$$

(a) What are the units on surface tension γ?

(b) Verify equation 6.24 above by taking the derivative of A and V.

(c) Derive a new equation in terms of dV, using equation 6.24.

(d) If a spontaneous change in phase were to be accompanied by a positive dG value, does a large droplet radius or a small droplet radius contribute to a large dG value?

(e) Which evaporates faster, large droplets or small droplets?

(f) Does this explain the method of delivery of many perfumes and colognes via so-called atomizers?

6.6 & 6.7 Phase Diagrams, Phase Rule, and Natural Variables

6.32. Explain how glaciers, huge masses of solid ice, move. *Hint:* see equation 6.22.

6.33. Show that the units on either side of equations 6.18 and 6.19 are consistent.

6.34. Use a phase diagram to justify the concept that the liquid phase can be considered a "metastable" phase, depending on the pressure and temperature conditions of the system.

6.35. Use the phase diagram of water in Figure 6.6 and count the *total* number of phase transitions that are represented.

6.36. Figure 6.16 is the phase diagram of ^3He at very low temperatures:

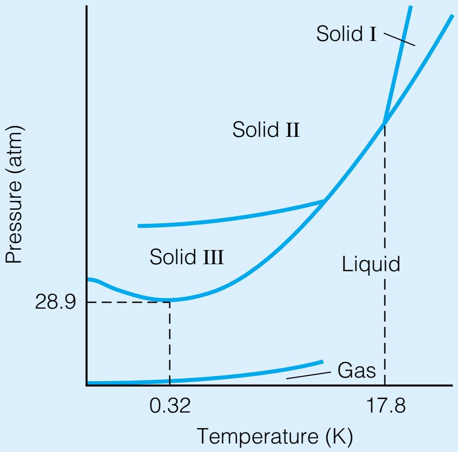


Figure 6.16 Phase diagram of ^3He. *Source:* Adapted from W. E. Keller, *Helium-3 and Helium-4*, Plenum Press, New York, 1969.

Notice that the slope of the solid-liquid equilibrium line below about 0.3 K is negative. Interpret this surprising experimental finding.

6.37. If a phase diagram were designed to have only a single axis, what would be the form of the phase rule for a single component? How many parameters would you have to specify to indicate the conditions of **(a)** a phase transition, or **(b)** the critical point?

6.38. If a material sublimes at normal atmospheric pressure, does one need higher or lower pressures to get that material in a liquid phase? Justify your answer.

6.39. Defining the critical point of a substance requires two degrees of freedom. (Those degrees of freedom are the critical temperature and the critical pressure.) Justify this fact in light of the Gibbs phase rule.

6.40. Refer to Figure 6.3, the unexpanded version of the phase diagram of H_2O. Label each line in the phase diagram in terms of what derivative it represents.

6.41. Repeat the previous exercise, only this time using Figure 6.6, the more complete phase diagram for H_2O.

6.42. The phase diagram for elemental sulfur is shown in Figure 6.17.

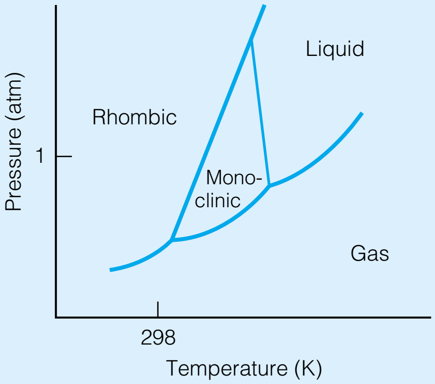


Figure 6.17 Phase diagram of elemental sulfur.

(a) How many allotropes are shown? **(b)** What is the stable allotrope of sulfur under normal conditions of temperature and pressure? **(c)** Describe the changes to sulfur as its temperature is increased from 25°C while at 1 atm pressure.

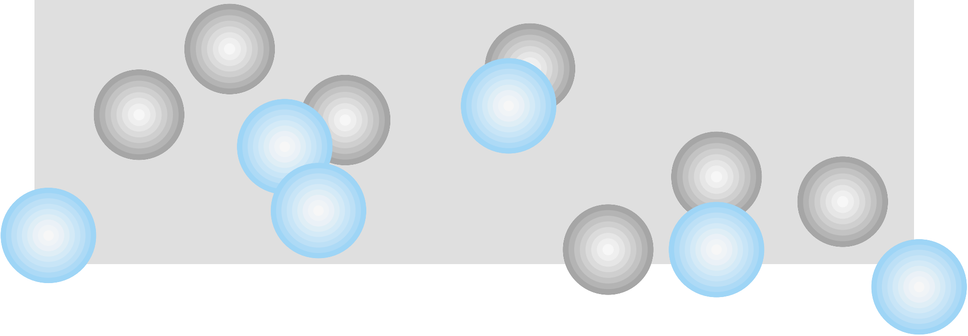
6.43. Consider the phase diagram of sulfur in the previous exercise. If one starts at 25°C and 1 atm pressure (which is about equal to 1 bar) and increases the temperature, comment on the entropy change as the sulfur goes from rhombic to monoclinic solid phases. Is it positive or negative? On the basis of the second law of thermodynamics, is the phase transition expected to be spontaneous?

Symbolic Math Exercises

6.44. Rearrange the Clausius-Clapeyron equation, equation 6.14, in terms of the pressure p_2 of a material. Plot the vapor pressures of H_2O (the boiling point is 100°C, $\Delta_{vap}H = 40.71$ kJ/mol), neon (the boiling point is -246.0°C, $\Delta_{vap}H = 1.758$ kJ/mol), and Li (the boiling point is 1342°C, $\Delta_{vap}H = 134.7$ kJ/mol). Although these three materials are very different, are there any similarities in the behavior of the vapor pressures as the temperature increases?

7

Equilibria in Multiple-Component Systems



IN THE PREVIOUS CHAPTER, we introduced some important concepts that we can apply to systems at equilibrium. The Clapeyron equation, the Clausius-Clapeyron equation, and the Gibbs phase rule are tools that are used to understand the establishment and changes of systems at equilibrium. However, so far we have considered only systems that have a single chemical component. This is very limiting, since most chemical systems of interest have more than one chemical component. They are *multiple*-component systems.

We will consider multiple-component systems in two ways. One way will be to extend some of the concepts of the previous chapter. We will do that only in a limited fashion. The other way will be to build on the previous chapter's ideas and develop new ideas (and equations) that apply to multiple-component systems. This will be our main approach.

7.1 Synopsis

We start by extending the Gibbs phase rule to multiple-component systems, in its most general form. We will confine our development of multiple-component systems to relatively simple ones, having two or three components at most. However, the ideas we will develop are generally applicable, so there will be little need to consider more complicated systems here. One example of a simple two-component system is a mixture of two liquids. We will consider that, as well as the characteristics of the vapor phase in equilibrium with the liquid. This will lead into a more detailed study of solutions, where different phases (solid, liquid, and gas) will act as either the solute or solvent.

The equilibrium behavior of solutions can be generalized by statements like Henry's law or Raoult's law, and can be understood in terms of activity rather than concentration. Changes in certain properties of all solutions can be understood simply in terms of the number of solvent and solute particles. These properties are called colligative properties.

Throughout the chapter, we will introduce new ways of graphically representing the behavior of multicomponent systems in an efficient visual way. New ways of drawing phase diagrams, some simple and some complex, will be presented.

7.2 The Gibbs Phase Rule

In the previous chapter, we introduced the Gibbs phase rule for a single component. Recall that the phase rule gives us the number of independent variables that must be specified in order to know the condition of an isolated system at equilibrium. For a single-component system, only the number of stable phases in equilibrium is necessary to determine how many other variables, or *degrees of freedom,* are required to specify the state of the system.

If the number of components is greater than one, then more information is necessary to understand the state of the system at equilibrium. Before we consider how much more information is necessary, let us review what information we do have. First, since we are assuming that the system is at equilibrium, then the system's temperature, T_{sys}, and the system's pressure, p_{sys}, are the same for all components. That is,

$$T_{\text{comp.1}} = T_{\text{comp.2}} = T_{\text{comp.3}} = \cdots = T_{\text{sys}} \tag{7.1}$$

$$p_{\text{comp.1}} = p_{\text{comp.2}} = p_{\text{comp.3}} = \cdots = p_{\text{sys}} \tag{7.2}$$

We also have the requirement, from the previous chapter, that the temperatures and pressures experienced by all phases are the same: $T_{\text{phase1}} = T_{\text{phase2}} = \cdots$ and $p_{\text{phase1}} = p_{\text{phase2}} = \cdots$. Equation 7.2 is not meant to imply that the *partial* pressures of individual gas components are the same. It means that every component of the system, even gaseous components, are subject to the same overall system pressure. We will also assume that our system remains at constant volume (is isochoric) and that we know the total amount of material, usually in units of moles, in our system. After all, the experimenter controls the initial conditions of the system, so we will always begin by knowing the initial amount of material.

With this understanding, how many degrees of freedom must be specified in order to know the state of a system at equilibrium? Consider a system that has a number of components C and a number of phases P. To describe the relative amounts (like mole fractions) of the components, $C - 1$ values must be specified. (The amount of the final component can be determined by subtraction.) Since the phase of each component must be specified, we need to know $(C - 1) \cdot P$ values. Finally, if temperature and pressure need to be specified, we have a total of $(C - 1) \cdot P + 2$ values that we need to know in order to describe our system.

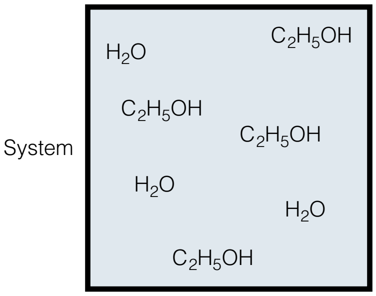
But if our system is at equilibrium, the chemical potentials of the different phases of each component must be equal. That is,

$$\mu_{1,\text{sol}} = \mu_{1,\text{liq}} = \mu_{1,\text{gas}} = \cdots = \mu_{1,\text{other phase}}$$

and this must hold for every component, not just component 1. This means we can remove $P - 1$ values for every component C, for a total of $(P - 1) \cdot C$ values. The number of values remaining represents the degrees of freedom, F: $(C - 1) \cdot P + 2 - (P - 1) \cdot C$, or

$$F = C - P + 2 \tag{7.3}$$

Equation 7.3 is the more complete *Gibbs phase rule.* For a single component, it becomes equation 6.17. Note that it is applicable only to systems at equilibrium. Also note that although there can be only one gas phase, due to the mutual solubility of gases in each other, there can be multiple liquid phases (that is, immiscible liquids) and multiple solid phases (that is, independent, nonalloyed solids in the same system).



Degrees of freedom at equilibrium:

- Temperature
- Pressure
- Amount (mole fraction) of one component (mole fraction of other can be determined)

∴ 3 degrees of freedom

From Gibbs phase rule:

$F = \underset{C}{2} - \underset{P}{1} + 2 = 3$ degrees of freedom ✓

Figure 7.1 A simple multiple-component system of water and ethanol. The Gibbs phase rule applies to this system, too.

What are the degrees of freedom that can be specified? We already know that pressure and temperature are common degrees of freedom. But for multiple-component systems, we also need to specify the relative amounts of each component, usually in terms of moles. Figure 7.1 illustrates this for a simple system.

If a chemical equilibrium is present, then not all of the components are truly independent. Their relative amounts are dictated by the stoichiometry of the balanced chemical reaction. Before applying the Gibbs phase rule, we need to identify the number of independent components. This is done by removing the *dependent* component from consideration. A dependent component is one that is made from any other component(s) in the system. In Figure 7.1, the water and ethanol are not in any chemical equilibrium involving both these compounds, so they are independent components. However, for the equilibrium

$$H_2O\ (\ell) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$$

the amounts of hydrogen and hydroxide ions are related by the chemical reaction. Thus, instead of having three independent components, we have only two: H_2O and either H^+ or OH^- (the other can be determined by the fact that the reaction is at equilibrium). Examples 7.1 and 7.2 illustrate degrees of freedom.

Example 7.1

Consider a mixed drink that has ethanol (C_2H_5OH), water, and ice cubes in it. Assuming that this describes your system, how many degrees of freedom are necessary to define your system? What might the degrees of freedom be?

Solution

There are two individual components: C_2H_5OH and H_2O. There are also two phases, solid (the ice cubes) and liquid (the water/ethanol solution). There are no chemical equilibria to consider, so we don't have to worry about dependencies among the components. Therefore, from the Gibbs phase rule, we have

$$F = C - P + 2 = 2 - 2 + 2$$

$$F = 2$$

What might be specified? If the temperature is specified, then we know the pressure of the system, because we also know that liquid and solid H_2O are in equilibrium. We can use the phase diagram of H_2O to determine the necessary pressure if the temperature is given. Another specification might be an amount of one component. We usually know a total amount of material in a system. By specifying one component's amount we can subtract to find the other component's amount. By specifying these two degrees of freedom, we completely define our system.

Example 7.2

Iron(III) sulfate, $Fe_2(SO_4)_3$, decomposes upon heating to make iron(III) oxide and sulfur trioxide by the following reaction:

$$Fe_2(SO_4)_3\ (s) \rightleftharpoons Fe_2O_3\ (s) + 3SO_3\ (g)$$

Using the phase labels given in the equilibrium reaction, how many degrees of freedom does this equilibrium have?

Solution

There are three distinct phases in this equilibrium, a solid ferric sulfate phase, a solid ferric oxide phase, and a gaseous phase. Therefore, $P = 3$. As with the H_2O dissociation, there are only two independent components in this equilibrium. (The amount of the third component can be determined from the stoichiometry of the reaction.) Therefore $C = 2$. Using the Gibbs phase rule,

$$F = 2 - 3 + 2$$

$$F = 1$$

7.3 Two Components: Liquid/Liquid Systems

An understanding of the Gibbs phase rule for multicomponent systems allows us to consider specific multicomponent systems. We will focus on two-component systems for illustration, although the concepts are applicable to systems with more than two components.

Let us consider a *binary* solution that is composed of two liquid components that are not interacting chemically. If the volume of the liquid is equal to the size of the system, then we have only one phase and two components, so the Gibbs phase rule says that we have $F = 2 - 1 + 2 = 3$ degrees of freedom. We can specify temperature, pressure, and mole fraction of one component to completely define our system. Recall from equation 3.22 that the mole fraction of a component equals the moles of some component i, n_i, divided by the total number of moles of all components in the system, n_{tot}:

$$\text{mole fraction of component } i \equiv x_i = \frac{n_i}{\sum\limits_{\text{all } i} n_i} = \frac{n_i}{n_{\text{tot}}} \tag{7.4}$$

The sum of all of the mole fractions for a phase in a system equals exactly 1. Mathematically,

$$\sum_i x_i = 1 \tag{7.5}$$

This is why we need specify only one mole fraction in our binary solution. The other mole fraction can be determined by subtraction.

If, however, the volume of liquid is less than the volume of the system, then there is some "empty" space in the system. This space is not empty but filled with the vapors of the liquid components. In all systems where the liquid volume is less than the system volume, *the remaining space will be filled with each component in the gas phase,* as shown in Figure 7.2.* If the system has a single component, then the partial pressure of the gas phase is characteristic of only two things: the identity of the liquid phase, and the temperature. This equilibrium gas-phase pressure is called the *vapor pressure* of the pure liquid. In a two-component liquid solution in equilibrium with its vapor, the chemical potential for each component in the gas phase must be equal to the chemical potential in the liquid phase:

$$\mu_i(\ell) = \mu_i(\text{g}) \quad \text{for } i = 1, 2$$

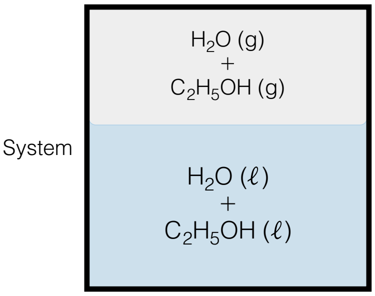


Figure 7.2 Systems with more volume than condensed phase will always have a vapor phase in equilibrium with that condensed phase. Although we usually picture liquid in equilibrium with vapor, in many cases solid phases also exist in equilibrium with a vapor phase.

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*In many cases, the same statement applies if the system has a solid phase that does not completely fill the system. "Freezer burn" is one example of this happening to solid H_2O.

According to equation 4.58, the chemical potential of a real gas is related to some standard chemical potential plus a correction factor in terms of the fugacity of the gas:

$$\mu_i\,(\mathrm{g}) = \mu_i^\circ\,(\mathrm{g}) + RT\ln\frac{f}{p^\circ} \tag{7.6}$$

where R and T have their usual thermodynamic definitions, f is the fugacity of the gas, and p° represents the standard condition of pressure (1 bar or 1 atm). For liquids (and, in appropriate systems, solids as well) there is an equivalent expression. However, instead of using fugacity, we will define the chemical potential of a liquid in terms of its *activity*, a_i, as introduced in Chapter 5:

$$\mu_i\,(\ell) = \mu_i^\circ\,(\ell) + RT\ln a_i \tag{7.7}$$

At equilibrium, the chemical potentials of the liquid and the vapor phases must be equal. From the above two equations,

$$\mu_i\,(\mathrm{g}) = \mu_i\,(\ell)$$

$$\mu_i^\circ\,(\mathrm{g}) + RT\ln\frac{f}{p^\circ} = \mu_i^\circ\,(\ell) + RT\ln a_i \quad i = 1, 2 \tag{7.8}$$

for each component i. (At this point, it is important to keep track of which terms refer to which phase, g or ℓ.) If we assume that the vapors are acting as ideal gases, then we can substitute the partial pressure, p_i, for the fugacity, f, on the left side. Making this substitution into equation 7.8:

$$\mu_i^\circ\,(\mathrm{g}) + RT\ln\frac{p_i}{p^\circ} = \mu_i^\circ\,(\ell) + RT\ln a_i \tag{7.9}$$

If the system were composed of a *pure* component, then the liquid phase would not need the second corrective term that includes the activity. For a single-component system, equation 7.9 would be

$$\mu_i^\circ\,(\mathrm{g}) + RT\ln\frac{p_i^\star}{p^\circ} = \mu_i^\circ\,(\ell) \tag{7.10}$$

where $p_i^\star$ is the equilibrium vapor pressure of the pure liquid component. Substituting for $\mu_i^\circ\,(\ell)$ from equation 7.10 into the right side of equation 7.9, we get

$$\mu_i^\circ\,(\mathrm{g}) + RT\ln\frac{p_i}{p^\circ} = \mu_i^\circ\,(\mathrm{g}) + RT\ln\frac{p_i^\star}{p^\circ} + RT\ln a_i$$

The standard chemical potential μ° (g) cancels. Moving both RT terms to one side, this equation becomes

$$RT\ln\frac{p_i}{p^\circ} - RT\ln\frac{p_i^\star}{p^\circ} = RT\ln a_i$$

We can cancel R and T from the equation, and then combine the logarithms on the left side. When we do this, the p°'s cancel. We get

$$\ln\frac{p_i}{p_i^\star} = \ln a_i$$

Taking the inverse logarithm of both sides, we find an expression for the activity of the liquid phase of the component labeled i:

$$a_i = \frac{p_i}{p_i^\star} \qquad i = 1, 2 \tag{7.11}$$

where p_i is the equilibrium vapor pressure above the solution and p_i^* is the equilibrium vapor pressure of the pure liquid. Equation 7.11 lets us determine the activities of liquids using equilibrium vapor pressures of gases.

Referring back to equation 7.9, the right side of the equation is simply the chemical potential, $\mu_i\,(\ell)$. For a two-component liquid in equilibrium with its vapor, each component must satisfy an expression like equation 7.9:

$$\mu_i\,(\ell) = \mu_i^\circ\,(\mathrm{g}) + RT\ln\frac{p_i}{p^\circ} \qquad i = 1, 2 \tag{7.12}$$

where we have reversed equation 7.9 as well as substituted $\mu_i\,(\ell)$. If the solution were ideal, then the amounts of vapor p_i of each component in the vapor phase would be determined by how much of each component was in the liquid phase. The more of one component in the liquid mixture, the more of its vapor would be in the vapor phase, going from $p_i = 0$ (corresponding to having no component i in the system) to $p_i = p_i^*$ (corresponding to all component i in the system). *Raoult's law* states that for an ideal solution, the partial pressure of a component, p_i, is proportional to its mole fraction of the component in the *liquid* phase. The proportionality constant is the vapor pressure of the pure component p_i^*:

$$p_i = x_i p_i^* \qquad i = 1, 2 \text{ for binary solution} \tag{7.13}$$

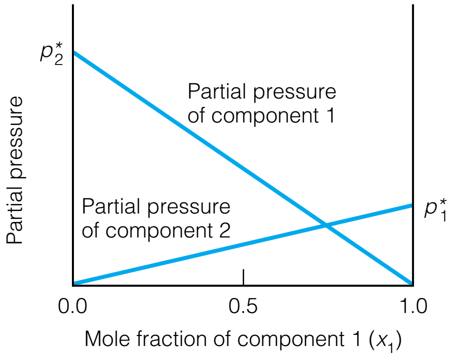

Figure 7.3 Raoult's law states that the partial pressure of a component in the gas phase that is in equilibrium with the liquid phase is directly proportional to the mole fraction of that component in the liquid. Each plot of partial pressure is a straight line. The slope of the straight line is p_i^*, the equilibrium vapor pressure of the pure liquid component.

Figure 7.3 shows a plot of the partial pressures of two components of a solution that follows Raoult's law. The straight lines between zero partial pressure and p_i^* are characteristic Raoult's-law behavior. (As required by the straight-line form of equation 7.13, the slope of each line is equal to the equilibrium vapor pressure of each component. The intercepts also equal p_i^* because the x-axis is mole fraction, which ranges from 0 to 1.) The following of Raoult's law is one requirement for defining an ideal solution; other requirements of an ideal solution will be presented at the end of this section.

If the solution is ideal, we can use Raoult's law to understand chemical potentials for liquids in equilibrium with their vapors in two-component systems. We rewrite equation 7.12 by substituting into the numerator for p_i:

$$\mu_i\,(\ell) = \mu_i^\circ\,(\mathrm{g}) + RT\ln\frac{x_i p_i^*}{p_i^\circ} \tag{7.14}$$

We can rearrange the logarithm term, isolating the characteristic values p_i^* (the equilibrium vapor pressure) and p_i° (the standard pressure):

$$\mu_i\,(\ell) = \mu_i^\circ\,(\mathrm{g}) + RT\ln\frac{p_i^*}{p_i^\circ} + RT\ln x_i$$

The first two terms on the right side are characteristic of the component and are constant at a given temperature; we group them together into a single constant term $\mu_i'\,(\mathrm{g})$:

$$\mu_\mathrm{i}'\,(\mathrm{g}) \equiv \mu_i^\circ\,(\mathrm{g}) + RT\ln\frac{p_i^*}{p_i^\circ} \tag{7.15}$$

Substituting, we find a relationship for the chemical potential of a liquid in an ideal solution:

$$\mu_i\,(\ell) = \mu_i'\,(\mathrm{g}) + RT\ln x_i \qquad i = 1, 2 \tag{7.16}$$

Chemical potentials of liquids are thus related to their mole fractions in multiple-component systems.

Raoult's law is useful in understanding the vapor-phase behavior of ideal solutions. If the vapor phase is treated as an ideal gas, then Dalton's law of partial pressures says that the total pressure is the sum of the individual partial pressures. For our two-component system, this becomes

$$p_{\text{tot}} = p_1 + p_2$$

From Raoult's law, this becomes

$$p_{\text{tot}} = x_1 p_1^{\star} + x_2 p_2^{\star}$$

However, x_1 and x_2 are not independent: since the sum of the mole fractions of the liquid phase must equal 1, we have $x_1 + x_2 = 1$, or $x_2 = 1 - x_1$. We can substitute:

$$p_{\text{tot}} = x_1 p_1^{\star} + (1 - x_1) p_2^{\star}$$

We can algebraically rearrange this:

$$p_{\text{tot}} = p_2^{\star} + (p_1^{\star} - p_2^{\star}) x_1 \tag{7.17}$$

This expression has the form of a straight line, $y = mx + b$. In this case, x_1 represents the mole fraction of component 1 in the *liquid* phase. If we plot total pressure versus mole fraction of component 1, we would get a straight line as shown in Figure 7.4. The slope would be $p_1^{\star} - p_2^{\star}$, and the y-intercept would be $p_2^{\star}$. Figure 7.4 suggests that there is a smooth, linear variation in total vapor pressure from $p_1^{\star}$ to $p_2^{\star}$ as the composition of the solution varies. Figure 7.4 also shows, in dotted lines, the individual partial pressures. Compare this to Figure 7.3.

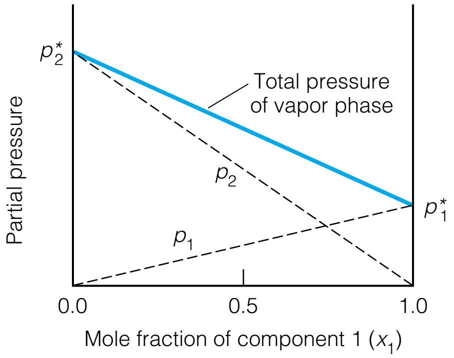

Figure 7.4 The total pressure of an ideal liquid solution is a smooth transition from one pure vapor pressure to the other.

Example 7.3

An ideal solution can be approximated using the liquid hydrocarbons hexane and heptane. At 25°C, hexane has an equilibrium vapor pressure of 151.4 mmHg and heptane has an equilibrium vapor pressure of 45.70 mmHg. What is the equilibrium vapor pressure of a 50:50 molar hexane and heptane solution (that is, $x_1 = x_2 = 0.50$) in a closed system? It does not matter which liquid is labeled 1 or 2.

Solution

Using Raoult's law, we have

$$p_1 = (0.50)(151.4 \text{ mmHg}) = 75.70 \text{ mmHg}$$

$$p_2 = (0.50)(45.70 \text{ mmHg}) = 22.85 \text{ mmHg}$$

By Dalton's law, the total vapor pressure in the system is the sum of the two partial pressures:

$$p_{\text{tot}} = 75.70 + 22.85 \text{ mmHg} = 98.55 \text{ mmHg}$$

Since boiling of a liquid occurs when the vapor pressure of a liquid equals the surrounding pressure, liquid solutions will boil at different temperatures depending on their composition and the vapor pressures of the pure components. The next example illustrates how this idea can be used.

Example 7.4

In analogy to ice baths, there are vapor baths that are kept at constant temperature by the equilibrium between the liquid and gas phases. A hexane/heptane solution is used to establish a constant 65°C temperature in a closed system that has a pressure of 500.0 mmHg. At 65°, the vapor pressures of hexane and heptane are 674.9 and 253.5 mmHg. What is the composition of the solution?

Solution

If we are seeking the composition of the solution, we need to determine one of the mole fractions of the liquid phase, say x_1. We can find x_1 by rearranging equation 7.17 algebraically:

$$x_1 = \frac{p_{\text{tot}} - p_2^*}{p_1^* - p_2^*}$$

We have all the information needed: $p_1^* = 674.9$ mmHg, $p_2^* = 253.5$ mmHg, and $p_{\text{tot}} = 500$ mmHg. Substituting and solving:

$$x_1 = \frac{500.0 \text{ mmHg} - 253.5 \text{ mmHg}}{674.9 \text{ mmHg} - 253.5 \text{ mmHg}} = \frac{246.5 \text{ mmHg}}{421.4 \text{ mmHg}}$$

Notice that the units of mmHg will cancel, leaving a unitless value. Mole fractions are unitless, so this is as it should be. We get

$$x_1 = 0.5850$$

which suggests that our liquid mixture is a little over half hexane. The mole fraction of heptane would be $1 - 0.5850 = 0.4150$, just less than half.

What are the mole fractions of the two components in the *vapor* phase? They are not equal to the mole fractions of the liquid phase. We use the variables y_1 and y_2 to represent the *vapor-phase mole fractions.*[†] They can be determined using Dalton's law, the idea that the mole fraction of a component in a gas mixture is equal to its partial pressure divided by the total pressure:

$$y_1 = \frac{p_1}{p_{\text{tot}}} = \frac{p_1}{p_1 + p_2} = \frac{x_1 p_1^*}{x_1 p_1^* + x_2 p_2^*} \tag{7.18}$$

In the last expression, we used Raoult's law to substitute in terms of p_1^* and p_2^*. Again, we note that $x_2 = 1 - x_1$, so we can substitute into equation 7.18 to get

$$y_1 = \frac{x_1 p_1^*}{x_1 p_1^* + (1 - x_1) p_2^*}$$

which rearranges to

$$y_1 = \frac{x_1 p_1^*}{p_2^* + (p_1^* - p_2^*) x_1} \tag{7.19}$$

Similarly, the mole fraction of component 2 is

$$y_2 = \frac{x_2 p_2^*}{x_1 p_1^* + x_2 p_2^*} \tag{7.20}$$

[†] For solutions and their vapor phases, the convention is to use x_i to represent the solution-phase mole fractions, and y_i to represent the vapor-phase mole fractions.

Similar substitutions can be made into equation 7.20 to get an expression like equation 7.19. As an example, for the 0.5850/0.4150 mixture of hexane and heptane in Example 7.4, the gas-phase mole fractions are 0.790 and 0.210, respectively, using equations 7.19 and 7.20. Note how different the mole fractions in the gas phase are from the mole fractions in the liquid phase.

We can take a slightly different perspective and derive an expression for the total pressure p_{tot} above the solution in terms of *vapor*-phase composition. For ideal gases, the partial pressure of a gas in a mixture is equal to the total pressure times the gas's mole fraction:

$$p_i = y_i p_{\text{tot}} \tag{7.21}$$

We can combine this with Raoult's law and its definition of the partial pressure of a gas-phase component to get

$$y_i p_{\text{tot}} = x_i p_i^\star$$

This equation relates the total pressure p_{tot}, the vapor pressure of the ith component $p_i^\star$, and the mole fractions of the ith component in the liquid phase (x_i) and the gas phase (y_i). Solving for p_{tot}:

$$p_{\text{tot}} = \frac{x_i p_i^\star}{y_i} \tag{7.22}$$

To be consistent with Figure 7.4, let us assume that $i = 1$. If we solve equation 7.19 for x_1, we get

$$x_1 = \frac{y_1 p_2^\star}{p_1^\star + (p_2^\star - p_1^\star)y_1} \tag{7.23}$$

We do this because we want to be able to express p_{tot} in terms of the mole fractions of the *vapor*, not the liquid, so we need to eliminate x_1. Substituting equation 7.23 into equation 7.22, we find that

$$p_{\text{tot}} = \frac{\dfrac{y_1 p_2^\star}{p_1^\star + (p_2^\star - p_1^\star)y_1}\, p_i^\star}{y_1}$$

$$p_{\text{tot}} = \frac{y_1 p_2^\star p_1^\star}{[p_1^\star + (p_2^\star - p_1^\star)y_1]y_1}$$

The y_1 terms in the numerator and denominator cancel, and we have for our final expression

$$p_{\text{tot}} = \frac{p_2^\star p_1^\star}{p_1^\star + (p_2^\star - p_1^\star)y_1} \tag{7.24}$$

A similar expression can be determined in terms of y_2 instead of y_1.

There is a key point about equation 7.24. It is similar to equation 7.17 in that we can plot the total pressure of the vapor phase with respect to the mole fraction of one component, y_1. However, it is not an equation for a straight line! Instead, it is an equation for a curved line, and if p_{tot} is plotted versus y_1 on the same scale as Figure 7.4, this line typically lies underneath the straight line of p_{tot} versus x_1. Figure 7.5 shows what this plot of p_{tot} versus y_1 looks like relative to p_{tot} versus x_1. The plot of p_{tot} versus x_1, the liquid mole fraction, is called the *bubble point line* whereas the plot of p_{tot} versus y_1, the vapor mole fraction, is called the *dew point line.* Diagrams like Figure 7.5, which plot vapor pressure versus mole fraction, are called *pressure-composition phase diagrams.*

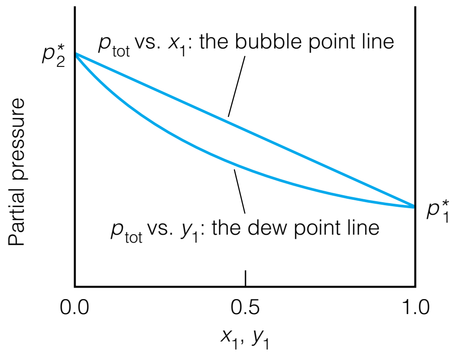

Figure 7.5 The mole fractions in the vapor phase are not the same as in the liquid phase. The bubble point line gives total pressure versus liquid-phase mole fraction, x_i. The dew point line gives total pressure versus vapor-phase mole fraction, y_i. The two lines would coincide only if both components had the same pure vapor pressure.

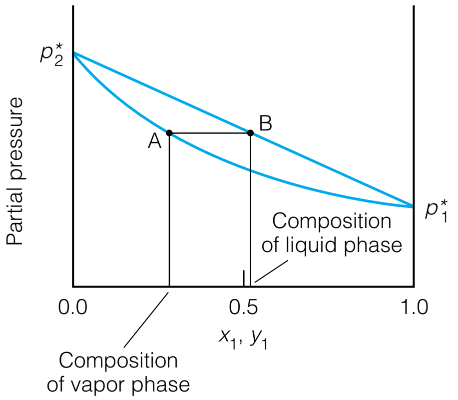

Figure 7.6 A horizontal tie line in a pressure-composition phase diagram like this connects the liquid-phase composition with the composition of the vapor phase that is in equilibrium.

Say you have a system with a particular liquid-phase composition. It will have a characteristic vapor-phase composition, determined by the expressions above. We can use pressure-composition phase diagrams like Figure 7.5 to represent the connection between the liquid-phase composition and the vapor-phase composition. A horizontal line in a diagram like Figure 7.5 represents a constant-pressure or isobaric condition. Figure 7.6 shows a horizontal line, segment AB, connecting the bubble point line and the dew point line for a liquid that has a certain mole fraction x_1. For a liquid having the composition indicated, the equilibrium vapor pressure for that liquid is found by going up the diagram until you intersect the bubble point line at point B. However, at that equilibrium pressure, the composition of the *vapor* phase is found by moving horizontally until you intersect the dew point line at point A. Such graphical representations are very useful in understanding how liquid-phase and vapor-phase compositions are related.

Example 7.5

At some particular temperature, the vapor pressure of pure benzene, C_6H_6, is 0.256 bar and the vapor pressure of pure toluene, $C_6H_5CH_3$, is 0.0925 bar. If the mole fraction of toluene in the solution is 0.600 and there is some empty space in the system, what is the total vapor pressure in equilibrium with the liquid, and what is the composition of the vapor in terms of mole fraction?

Solution

Using Raoult's law, we can determine the partial pressures of each component:

$$p_{\text{benzene}} = (0.400)(0.256\text{ bar}) = 0.102\text{ bar}$$

$$p_{\text{toluene}} = (0.600)(0.0925\text{ bar}) = 0.0555\text{ bar}$$

The total pressure is the sum of the two partial pressures:

$$p_{\text{tot}} = 0.102\text{ bar} + 0.0555\text{ bar} = 0.158\text{ bar}$$

We could also have used equation 7.17, letting toluene be component 1:

$$p_{\text{tot}} = 0.256 + (0.0925 - 0.256)0.60$$

$$p_{\text{tot}} = 0.158\text{ bar}$$

In order to determine the composition of the vapor (in mole fraction), we can use Dalton's law of partial pressures to set up the following:

$$y_{\text{toluene}} = \frac{0.0555\text{ bar}}{0.158\text{ bar}} = 0.351$$

$$y_{\text{benzene}} = \frac{0.102\text{ bar}}{0.158\text{ bar}} = 0.646$$

(The two mole fractions do not add up to exactly 1 because of truncation errors.) Notice that the vapor phase has been enriched in benzene over the original solution. This should make sense, given that benzene has a much higher vapor pressure than toluene.

Referring to Figure 7.6, note that point B is *not the boiling point* of the solution having that composition. It is simply the vapor pressure of the solution

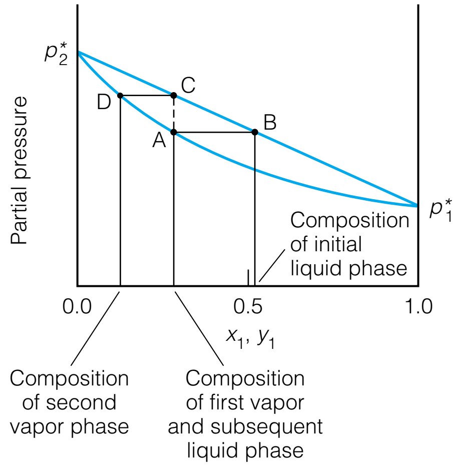

Figure 7.7 A vapor phase will condense into a liquid having the exact same composition, line AC. But that new liquid will not vaporize into a vapor having the same composition; rather, this new liquid will be in equilibrium with a vapor having composition D.

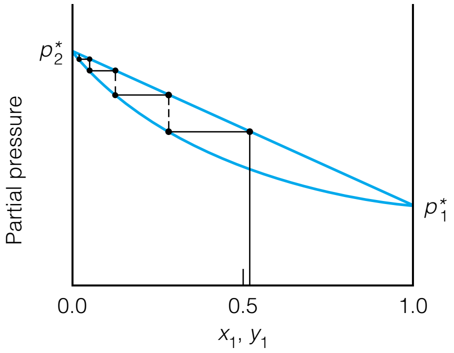

Figure 7.8 With repeated condensations and evaporations, eventually a pure liquid can be separated from the system. This is called fractional distillation.

at that composition. Only when the vapor pressure reaches the surrounding pressure will the two-component liquid be at its boiling point. (This detail is important only for systems that are open and exposed to some external pressure p_{ext}.)

Line AB in Figure 7.6 is called a *tie line.* It connects the liquid-phase composition with the resulting vapor-phase composition of the two components in the system.

Suppose your system is set up in a way that you can condense the vapor phase in a smaller subsystem. What would the composition of the new liquid phase be? If you're just condensing the vapors, then the composition of the new liquid phase would be exactly the same as the original vapor phase. Figure 7.7 shows that this new liquid phase can be represented on the bubble point line at point C. But now this subsequent liquid phase also has an equilibrium vapor phase, whose composition is given by the tie line CD in Figure 7.7. This second vapor phase is even more enriched in one component. If your system is set up to allow for multiple evaporations and condensations, each step between the bubble point line and the dew point line generates a vapor and subsequent liquid phase that are progressively richer and richer in one component. If the system is set up properly, ultimately you will get liquid and vapor phases that are essentially pure single component. The steps leading to this pure component are shown in Figure 7.8. What has happened is that we have started from the two-component mixture and have separated one component from the other. Such a procedure is called *fractional distillation,* and it is particularly common in organic chemistry. Each individual step, represented by a pair of horizontal and vertical lines, is called a *theoretical plate.* In practice, systems that are set up to perform fractional distillations can have as few as three or as many as tens of thousands of theoretical plates.

Figure 7.9 shows three setups for performing fractional distillations. The first two are apparatus that you might see in lab, using either macroscale or microscale glassware. The last is a fractional distillation apparatus on an industrial scale.

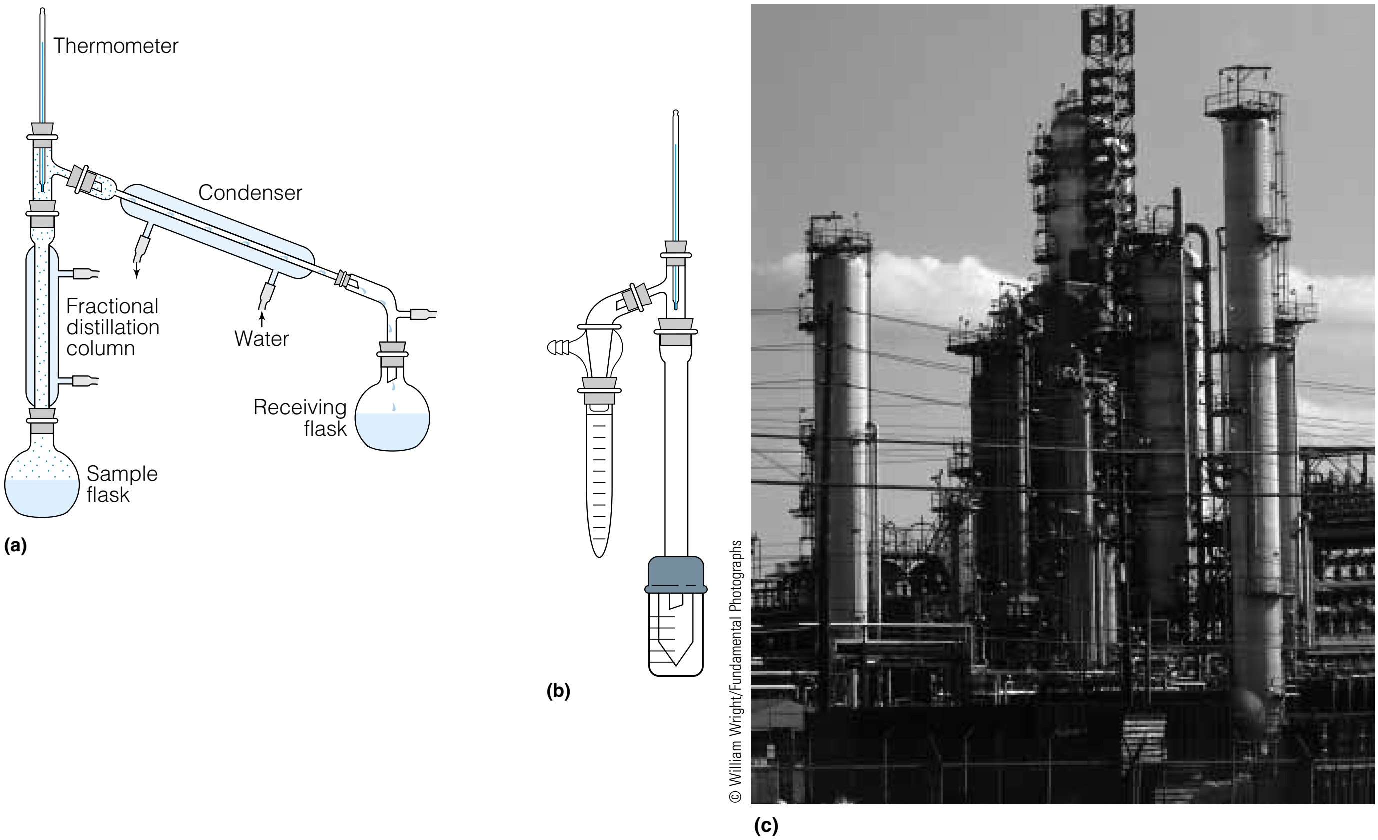

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Figure 7.9 Some fractional distillation apparatus. (a) A laboratory scale fractional distillation apparatus. (b) A microscale fractional distillation setup. Microscale equipment uses small amounts, so it is appropriate when only small amounts of material are available. (c) Fractional distillation on an industrial scale is a common process. This shows the hardware for large-scale distillations.

Fractional distillations are among the most important and energy-demanding processes, especially in the petrochemical industry.

Phase diagrams can also be plotted in terms of temperature—usually the boiling point (BP) of the liquid—versus composition. However, unlike the pressure-composition phase diagram, there is no simple straight-line equation to express one of the lines, so in temperature-composition phase diagrams both bubble point and dew point lines are curved. An example is shown in Figure 7.10, which corresponds to Figure 7.5. Notice that the higher component of vapor pressure, component 2, has the lower boiling point for the pure

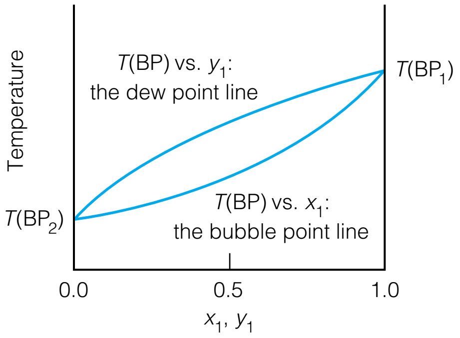

Figure 7.10 Temperature-composition phase diagrams are more common than pressure-composition diagrams. Notice, however, that neither line is straight, and that the lines indicating the boiling process and the condensation process are switched from the pressure-composition diagrams. Compare to Figure 7.5.

component. Also note that the bubble point line and the dew point line have switched places.

Fractional distillations can also be illustrated using temperature-composition phase diagrams. A solution of initial composition vaporizes into a vapor having a different composition. If this vapor is cooled, it condenses into a liquid having the same composition. This new liquid can establish an equilibrium with another vapor having a more enriched composition, which condenses, and so on. Figure 7.11 illustrates the stepwise process. Three theoretical plates are shown explicitly.

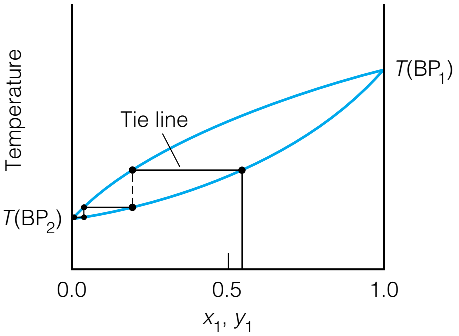

Figure 7.11 Fractional distillations can also be represented using temperature-composition phase diagrams. This diagram shows the same process as Figure 7.8. Can you explain the differences between the two representations of the same process?

Raoult's law is one requirement for an ideal liquid solution. There are a few other requirements for an ideal solution. When two pure components are mixed, there should be no change in the total internal energy or enthalpy of the components:

$$\Delta_{\text{mix}}U = 0 \tag{7.25}$$

$$\Delta_{\text{mix}}H = 0 \tag{7.26}$$

If the solution is mixed under conditions of constant pressure (which is usually an applicable restriction), then equation 7.26 implies that

$$q_{\text{mix}} = 0$$

Mixing is usually a spontaneous process, which means that $\Delta_{\text{mix}}S$ and $\Delta_{\text{mix}}G$ for the process must have the proper magnitudes. Indeed, in analogy to gas mixtures, for ideal liquids they are

$$\Delta_{\text{mix}}G = RT\sum_i x_i \ln x_i \tag{7.27}$$

$$\Delta_{\text{mix}}S = -R\sum_i x_i \ln x_i \tag{7.28}$$

for constant-temperature processes. Since x_i is always less than 1, the logarithms of x_i are always negative, so $\Delta_{\text{mix}}G$ and $\Delta_{\text{mix}}S$ will always be negative and positive, respectively. Mixing is a spontaneous, entropy-driven process. When one uses equations 7.27 and 7.28 and the units come out as joules per mole, the "per mole" part refers to the moles of components in the system. To calculate a total quantity, the amount per mole must be multiplied by the number of moles in the system, as shown in the following example.

Example 7.6

What are $\Delta_{\text{mix}}H$, $\Delta_{\text{mix}}U$, $\Delta_{\text{mix}}G$, and $\Delta_{\text{mix}}S$ for a system that mixes 1.00 mol of toluene and 3.00 mol of benzene? Assume ideal behavior and 298 K.

Solution

By definition, $\Delta_{\text{mix}}H$ and $\Delta_{\text{mix}}U$ are exactly zero. The total number of moles in our system is 4.00 mol, so for $\Delta_{\text{mix}}G$, we use $x_1 = 0.250$ and $x_2 = 0.750$. Therefore,

$$\Delta_{\text{mix}}G = \left(8.314\,\frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298\text{ K})(0.250 \cdot \ln 0.250 + 0.750 \cdot \ln 0.750)$$

$$\Delta_{\text{mix}}G = -1390\text{ J/mol} \cdot 4.00\text{ mol} = -5560\text{ J}$$

Similarly, for $\Delta_{\text{mix}}S$:

$$\Delta_{\text{mix}}S = -\left(8.314\ \frac{\text{J}}{\text{mol·K}}\right)(0.250 \cdot \ln 0.250 + 0.750 \cdot \ln 0.750)$$

$$\Delta_{\text{mix}}S = 4.68\ \frac{\text{J}}{\text{mol·K}} \cdot 4.00\ \text{mol} = 18.7\ \text{J/K}$$

Both state functions show that mixing will be spontaneous.

Notice that $\Delta_{\text{mix}}G$ and $\Delta_{\text{mix}}S$ satisfy the general equation

$$\Delta_{\text{mix}}G = \Delta_{\text{mix}}H - T\,\Delta_{\text{mix}}S$$

With $\Delta_{\text{mix}}H = 0$ for an ideal solution, this equation simplifies to

$$\Delta_{\text{mix}}G = -T\,\Delta_{\text{mix}}S \qquad \textbf{(7.29)}$$

There is usually one other requirement for the mixing of ideal solutions:

$$\Delta_{\text{mix}}V = 0 \qquad \textbf{(7.30)}$$

Of all requirements for an ideal solution, it is probably equation 7.30 that is most easily demonstrated to fail for most real liquid solutions. Most people are familiar with the example of pure water and pure alcohol. If 1.00 L of pure water is mixed with 1.00 L of pure alcohol, the resulting solution will be somewhat *less* than 2.00 L in volume.

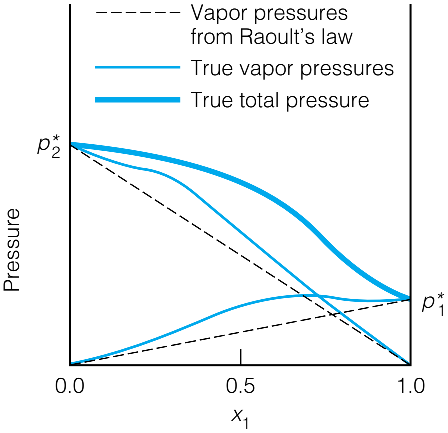

Figure 7.12 A nonideal solution showing a positive deviation from Raoult's law. Compare this to Figure 7.4.

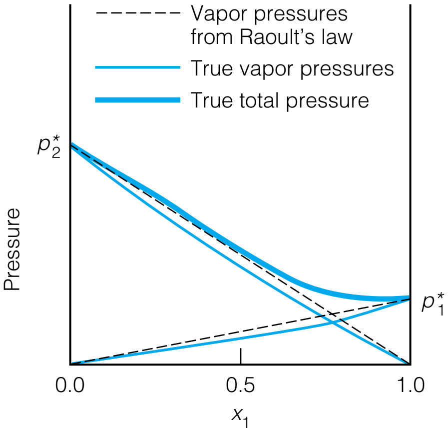

Figure 7.13 A nonideal solution showing a negative deviation from Raoult's law. Compare this, too, to Figure 7.4.

7.4 Nonideal Two-Component Liquid Solutions

Even simple two-component mixtures are not ideal, as suggested by the comment about $\Delta_{\text{mix}}V$ for solutions. Molecules in a liquid interact with each other, and molecules interact differently with liquid molecules of another species. These interactions cause deviations from Raoult's law. If the individual vapor pressures are higher than expected, the solution shows a *positive deviation* from Raoult's law. If the individual vapor pressures are lower than expected, then the solution shows a *negative deviation* from Raoult's law. The liquid-vapor phase diagrams for each case show some interesting behavior.

Figure 7.12 shows a liquid-vapor phase diagram for positive deviations from Raoult's law. Each component has a higher-than-expected vapor pressure, so the total pressure in equilibrium with the liquid solution is also higher than expected. Ethanol/benzene, ethanol/chloroform, and ethanol/water are systems that show a positive deviation from Raoult's law. Figure 7.13 shows a similar diagram, but for a solution that shows a negative deviation from Raoult's law. The acetone/chloroform system is one example that exhibits such nonideal behavior.

For plots of x_i and y_i versus composition, it is sometimes easier to use temperature-composition phase diagrams rather than pressure-composition phase diagrams. Figure 7.14 shows a positive deviation from Raoult's law. (Be sure to keep track of what the "positive" means: that the vapor pressure is higher than expected from Raoult's law. With the temperature and pressure being inversely related, a positive deviation from Raoult's law leads to a lower temperature for the boiling point, which is what Figure 7.14 illustrates.)

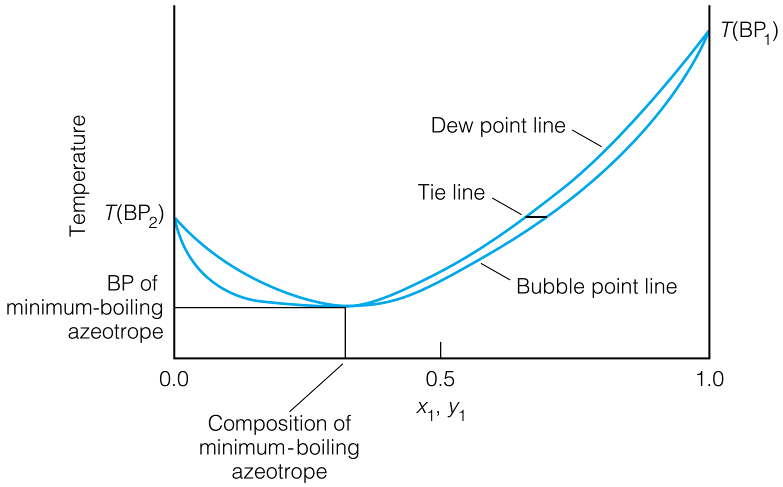

Figure 7.14 Temperature-composition phase diagram for a nonideal solution showing a positive deviation from Raoult's law. Notice the appearance of a point in which liquid and vapor have the same composition.

Figure 7.14 shows plots of composition of liquid and vapor phase versus temperature. The curious thing about this plot is that the bubble point line and the dew point line touch each other at one point, then separate again. At this point, the composition of the liquid and the composition of the vapor in equilibrium with the liquid have the exact same mole fraction. At this composition, the system is acting as if it were a single, pure component. This composition is called the *azeotropic composition* of the solution, and the "pure component" having this composition is called the *azeotrope.* In the case of Figure 7.14, since the azeotrope has a minimum temperature, it is called the *minimum-boiling azeotrope.* For example, H_2O and ethanol have a minimum-boiling azeotrope that boils at 78.2°C and is 96% ethanol and 4% water. (The normal boiling point of pure ethanol is just slightly higher at 78.3°C.)

Figure 7.15 shows a temperature-composition phase diagram for a negative deviation from Raoult's law. Again, there is a point where the bubble and dew point lines touch, in this case forming a *maximum-boiling azeotrope.* Since we

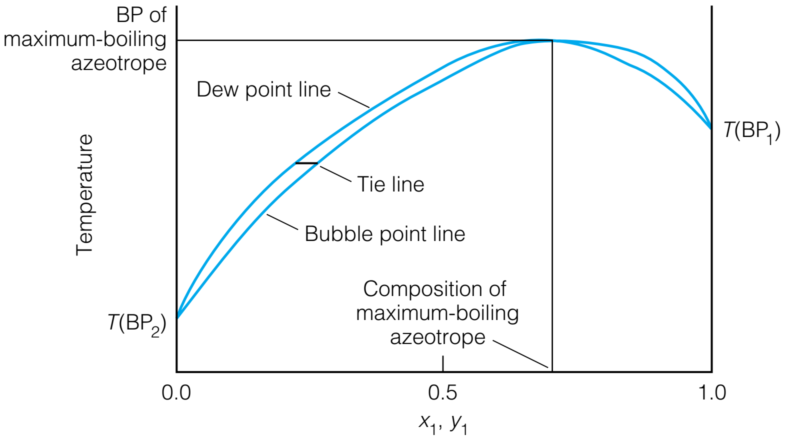

Figure 7.15 Temperature-composition phase diagram for a nonideal solution showing negative deviation from Raoult's law. The azeotrope is maximum-boiling, rather than minimum-boiling as shown in Figure 7.14.

are limiting our systems to two components, these azeotropes are all binary azeotropes, but in systems that have more than two components, there are also ternary azeotropes, quaternary azeotropes, and so forth. Almost all real systems have azeotropes in their liquid-vapor phase diagrams, and there is always only one unique composition for an azeotrope for any set of components.

Fractional distillation for a system that has an azeotrope is similar to the process illustrated in Figure 7.11. However, as the tie lines move from one composition to another, eventually either a pure component is reached, or an azeotrope is reached. If an azeotrope is reached, then there will be *no further change in the composition of the vapor,* and *no further separation* of the two components will take place by means of distillation. (There are other ways to separate the components of an azeotrope, but not by straightforward distillation. Such is the conclusion of thermodynamics.)

Example 7.7

Using a temperature-composition phase diagram like Figure 7.14, predict the general composition of the ultimate distillation product if a solution having a mole fraction x_1 of 0.9 is distilled.

Solution

Refer to Figure 7.16. Using the tie lines to connect the vapor composition for each liquid phase composition, we ultimately find ourselves at the minimum-boiling azeotrope. Therefore, the azeotrope is our ultimate product and no further separation can be performed using distillation.

As an additional example, what is the expected outcome if the solution has an initial mole fraction x_1 of 0.1?

Example 7.8

Using a temperature-composition phase diagram like Figure 7.15, predict the general composition of the ultimate distillation product if a solution having a mole fraction x_1 of 0.5 is distilled.

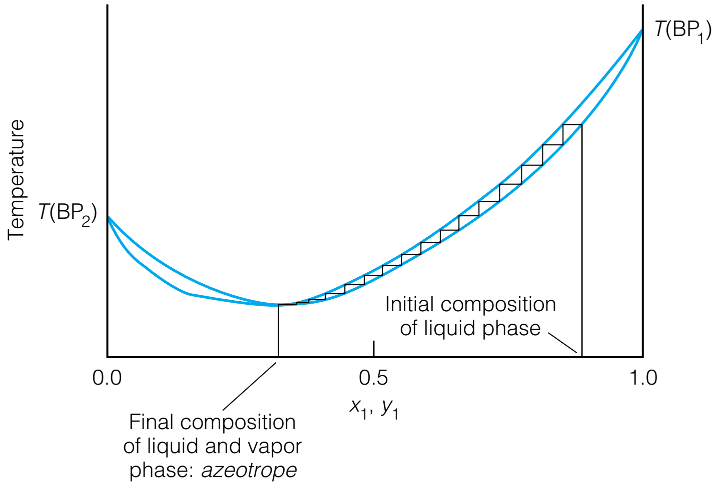

Figure 7.16 See Example 7.7. If one starts with a liquid having the composition indicated, the minimum-boiling azeotrope is the ultimate product.

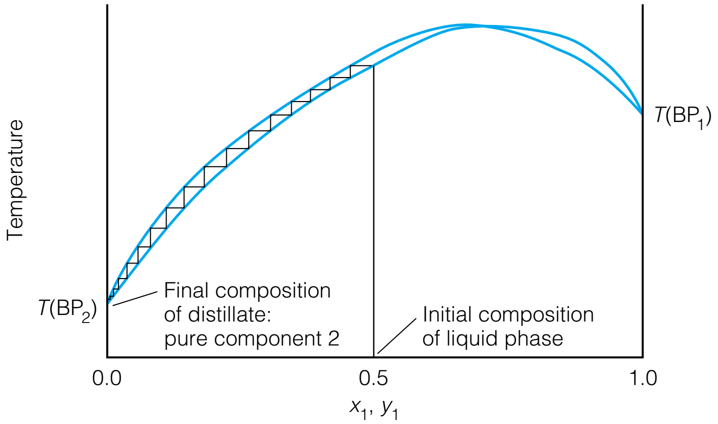

Figure 7.17 See Example 7.8. If one starts with a liquid having the composition indicated, the ultimate product will be one of the pure components.

Solution

Refer to Figure 7.17. Using the tie lines to connect the vapor composition for each liquid phase composition, we ultimately find ourselves at a composition consisting of $x_1 = 0$. Therefore, the pure component 2 is our ultimate product.

As an additional example, what is the expected outcome if the solution had an initial mole fraction x_1 of 0.1? Is your conclusion the same as the conclusion for the additional example in Example 7.7?

If deviations from ideality are large enough, then two liquids won't even make a solution at certain mole fractions: they will be *immiscible.* As long as there is enough of each component to establish an equilibrium with a vapor phase in the system, the pressure-composition phase diagram will look something like Figure 7.18. Between points A and B, we are implying that the two

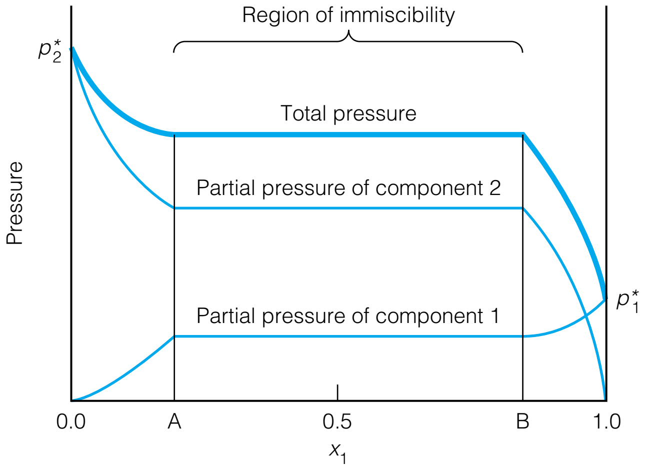

Figure 7.18 For very nonideal solutions, there may be ranges of immiscibility. In those ranges, the vapor composition will not change. Here, the region between points A and B is a region of immiscibility. The vapor pressure is constant in that range.

liquids are immiscible, so the total pressure in equilibrium with the liquids is simply the sum of the two equilibrium vapor pressures.*

7.5 Liquid/Gas Systems and Henry's Law

Gases can dissolve in liquids. In fact, liquid/gas solutions are important to us. One example is a soft drink, which has carbon dioxide gas dissolved in water. Another example is the ocean, where the solubility of oxygen is crucial to fish and other animal life, and the solubility of carbon dioxide is important for algae and other plant life. In fact, the ability of the oceans to dissolve gases is largely unknown but is thought to be a major factor in the weather conditions of the troposphere (the layer of the atmosphere closest to the surface of the earth).

Liquid/gas solutions range between extremes. Hydrogen chloride gas, HCl, is very soluble in water, making solutions of hydrochloric acid. By contrast, the solubility of 1 bar of pure oxygen in water is only about 0.0013 M.

Since liquid/gas solutions are nonideal, Raoult's law does not apply. This is illustrated in Figure 7.19, in which the vapor pressure of some gaseous component is plotted versus mole fraction. The figure shows a range of mole fraction where Raoult's law gives good predictions when compared to reality. However, this region is concentrated at large values of mole fraction; for most compositions, Raoult's law disagrees with real measurements.

However, Figure 7.19 does show that in regions of low mole fraction, the vapor pressure of the gas in the equilibrium vapor phase *is* proportional to the mole fraction of the component. This proportionality is illustrated by an approximately straight dotted line in the plot of pressure versus x_i at low mole fractions. Since the vapor pressure is proportional to the mole fraction, we can write this mathematically as

$$p_i \propto x_i$$

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*Here we are assuming that both liquids are exposed to some space within the system and can come to equilibrium with their vapor phases. In systems where a denser immiscible liquid is completely covered by a less dense liquid, its vapor pressure will be suppressed.

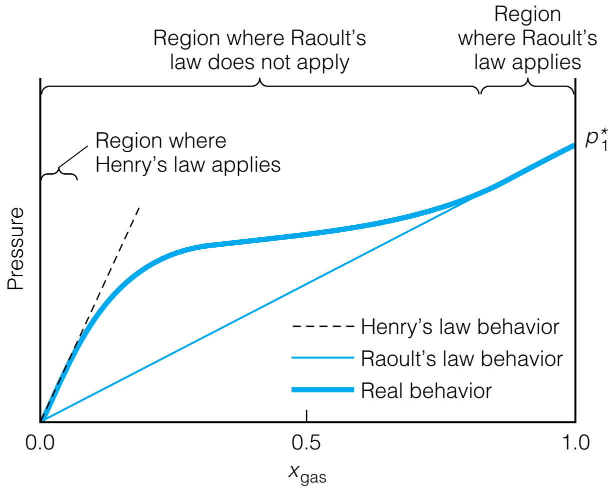

Figure 7.19 If a gas is one of the components, Raoult's law does not hold at low mole fractions of gas. However, there is a region of proportionality. This region can be described using Henry's law.

Table 7.1 Some Henry's law constants for aqueous solutions[a]

Compound	K_i (Pa)
Argon, Ar	4.03×10^9
1,3-Butadiene, C_4H_6	1.43×10^{10}
Carbon dioxide, CO_2	1.67×10^8
Formaldehyde, CH_2O	1.83×10^3
Hydrogen, H_2	7.03×10^9
Methane, CH_4	4.13×10^7
Nitrogen, N_2	8.57×10^9
Oxygen, O_2	4.34×10^9
Vinyl chloride, $CH_2{=}CHCl$	6.11×10^7

[a] Temperature is 25° C.

The way to make a proportionality an equality is to define a proportionality constant K_i, so now we have

$$p_i = K_i x_i \tag{7.31}$$

where the value of the constant K_i depends on the components and also the temperature. Equation 7.31 is called *Henry's law,* after the British chemist William Henry, who was a contemporary and friend of John Dalton (of modern atomic theory and Dalton's law of partial pressures fame). K_i is called the *Henry's law constant.*

Notice the similarity and difference between Raoult's law and Henry's law. Both apply to the vapor pressure of volatile components in a solution. Both say that the vapor pressure of one component is proportional to the mole fraction of that component. But whereas Raoult's law defines the proportionality constant as the vapor pressure of the pure component, Henry's law defines the proportionality constant as some experimentally determined value. Some Henry's law constants are listed in Table 7.1.

Many applications of Henry's law define the system from a different perspective. Instead of specifying the solution composition, the liquid phase and the equilibrium gas component pressure are specified. Then the question is asked, what is the equilibrium mole fraction of the gas in the resulting equilibrium solution? The following example illustrates.

Example 7.9

The Henry's law constant K_i for CO_2 in water is 1.67×10^8 Pa (Pa = pascal; 1 bar = 10^5 Pa) at some particular temperature. If the pressure of CO_2 in equilibrium with water were 1.00×10^6 Pa (which equals 10 bar, or about 10 atm) at that temperature, what is the mole fraction of CO_2 in the solution? Can you estimate the molarity of the CO_2 solution?

Solution

In this example, we are specifying the equilibrium partial pressure of the gas in the gas phase, and determining the mole fraction in the liquid solution (rather than the other way around, which has been the habit so far). Using equation 7.31, we have

$$1.00 \times 10^6 \text{ Pa} = (1.67 \times 10^8 \text{ Pa}) \cdot x_i$$

Solving, we find that

$$x_i = 0.00599$$

Notice that the units have canceled. This is expected for a mole fraction, which is unitless. Since the mole fraction of CO_2 is so small, we will assume that the volume of 1 mole of solution is the molar volume of water, which is 18.01 mL or 0.01801 L. We further approximate that the mole fraction of H_2O molecules is about 1.00, so that the number of moles of CO_2 dissolved in the water is 0.00599 mole. Therefore, the approximate molarity of the solution is

$$\frac{0.00599 \text{ mol}}{0.01801 \text{ L}} = 0.333 \text{ M}$$

The higher number for the molar concentration of this solution belies the tiny mole fraction in the liquid phase. Carbonated beverages are typically made by using this pressure of gaseous carbon dioxide.

7.6 Liquid/Solid Solutions

In this section, we will consider only solutions in which the liquid component has the majority mole fraction (the *solvent*) and the solid component has the minority mole fraction (the *solute*). We will also assume that the solid solute is non-ionic, because the presence of oppositely charged ions in solution affects the properties of the solution (which will be considered in the next chapter). There is also a consideration that is implicit in specifying a solid component: it contributes nothing to the vapor phase that is in equilibrium with the solution. One way of speaking of this is to state that the solid is a *nonvolatile* component. Solutions of this sort are therefore easy to separate by *simple distillation* of the only volatile component, the solvent, rather than the more complicated fractional distillation. Figure 7.20 shows two experimental setups for simple distillation. Compare these to Figure 7.9.

Having mentioned the liquid-gas phase change for the liquid component, what about the liquid-solid phase change? That is, what happens when the solution is frozen? Typically, the freezing point of a solution is not the same as the freezing point of the pure liquid, which is a topic discussed shortly. However, when liquid solidifies, *pure solid phase is formed.* The remaining liquid phase becomes more concentrated in solute, and this increase in concentration continues until the solution is saturated. Any further concentration causes precipitation of solute along with solidification of the solvent. This continues until all of the solute is precipitated and all of the liquid component is pure solid.

Most liquid/solid solutions do not make solutions in infinite ratios. Typically, there is a limit to how much solid can be dissolved in a given amount of liquid. At this limit, the solution is said to be *saturated.* The *solubility* represents the amount of solid that is dissolved in order to make a saturated solution, and is given in a wide variety of units. [A common unit for

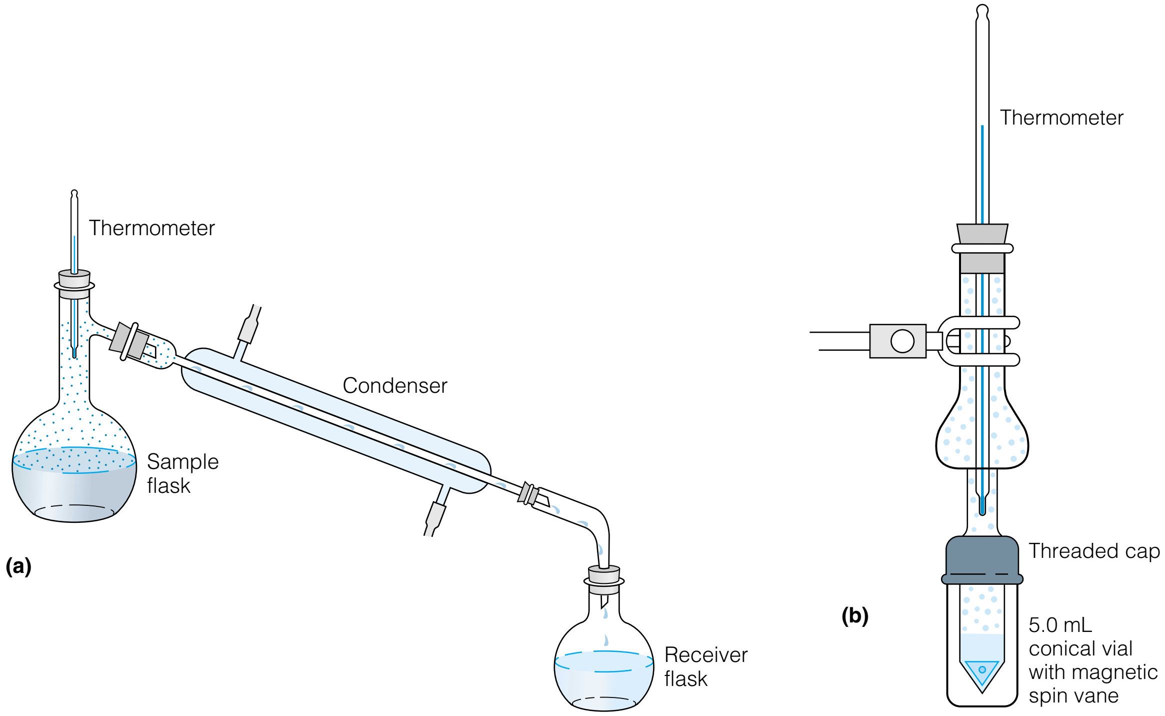

Figure 7.20 Apparatus for simple distillation. Compare these with Figure 7.9. (a) Normal-scale simple distillation apparatus. (b) Microscale simple distillation apparatus.

solubility is (grams of solute)/(100 mL of solvent).] Most of the solutions we work with are unsaturated, having less than the maximum amount of solute that can dissolve. Occasionally, it is possible to dissolve more than the maximum. This is typically done by heating the solvent, dissolving more solute, then cooling the solution carefully so that the excess solute does not precipitate. These are *supersaturated* solutions. However, they are not thermodynamically stable.

For an ideal liquid/solid solution, it is possible to calculate the solubility of the solid solute. If a saturated solution exists, then saturated solution is in equilibrium with excess, undissolved solute:

$$\text{solute (s)} + \text{solvent } (\ell) \rightleftharpoons \text{solute (solv)} \tag{7.32}$$

where the solute (solv) refers to the solvated solute, that is, the dissolved solid.

If this equilibrium does exist, then the chemical potential of the undissolved solid equals the chemical potential of the dissolved solute:

$$\mu^{\circ}_{\text{pure solute (s)}} = \mu_{\text{dissolved solute}} \tag{7.33}$$

The undissolved solute's chemical potential has a ° superscript because it is a pure material, whereas the chemical potential of the dissolved solute is part of a solution. However, if the dissolved solute can be considered as one component of a liquid/liquid solution (with the other liquid being the solvent itself), then the chemical potential of the dissolved solute is

$$\mu_{\text{dissolved solute}} = \mu^{\circ}_{\text{dissolved solute }(\ell)} + RT \ln x_{\text{dissolved solute}} \tag{7.34}$$

Substituting for $\mu_{\text{dissolved solute}}$ in equation 7.33:

$$\mu^{\circ}_{\text{pure solute (s)}} = \mu^{\circ}_{\text{dissolved solute }(\ell)} + RT \ln x_{\text{dissolved solute}} \tag{7.35}$$

This can be rearranged to find an expression for the mole fraction of the dissolved solute in solution:

$$\ln x_{\text{dissolved solute}} = \frac{\mu^{\circ}_{\text{pure solute (s)}} - \mu^{\circ}_{\text{pure solute }(\ell)}}{RT} \tag{7.36}$$

The expression in the numerator of equation 7.36 is the chemical potential of the solid minus the chemical potential of the liquid for a pure solute, which equals the change in the molar Gibbs free energy for the following process:

$$\text{solute } (\ell) \longrightarrow \text{solute (s)} \tag{7.37}$$

That is, the numerator refers to the change in free energy for a solidification process. The Gibbs free energy for this process would equal zero if it occurred at the melting point. If T is not the melting-point temperature, then $\Delta_{\text{fus}}G$ is not zero. Equation 7.37 is the reverse of the melting process, so the change in G can be represented as $-\Delta_{\text{fus}}G$. Therefore, equation 7.36 becomes

$$\ln x_{\text{dissolved solute}} = \frac{-\Delta_{\text{fus}}G}{RT} = \frac{-(\Delta_{\text{fus}}H - T\,\Delta_{\text{fus}}S)}{RT} \tag{7.38}$$

Here, we are substituting for $\Delta_{\text{fus}}G$, again noting that $\Delta_{\text{fus}}H$ and $\Delta_{\text{fus}}S$ represent the changes in enthalpy and entropy at some temperature T, which is not the melting point.

Now we will add zero to the last expression in equation 7.38, but in an unusual way: by adding $(\Delta_{\text{fus}}G_{\text{MP}})/RT_{\text{MP}}$, where $\Delta_{\text{fus}}G_{\text{MP}}$ is the Gibbs free energy of fusion and T_{MP} is the melting point of the solute. At the melting point, $\Delta_{\text{fus}}G_{\text{MP}}$ equals zero, so we are simply adding zero to equation 7.38. We get

$$\ln x_{\text{dissolved solute}} = \frac{-(\Delta_{\text{fus}}H - T\,\Delta_{\text{fus}}S)}{RT} + \frac{\Delta_{\text{fus}}G_{\text{MP}}}{RT_{\text{MP}}}$$

$$= \frac{-(\Delta_{\text{fus}}H - T\,\Delta_{\text{fus}}S)}{RT} + \frac{\Delta_{\text{fus}}H_{\text{MP}} - T_{\text{MP}}\,\Delta_{\text{fus}}S_{\text{MP}}}{RT_{\text{MP}}}$$

$$\ln x_{\text{dissolved solute}} = -\frac{\Delta_{\text{fus}}H}{RT} + \frac{\Delta_{\text{fus}}S}{R} + \frac{\Delta_{\text{fus}}H_{\text{MP}}}{RT_{\text{MP}}} - \frac{\Delta_{\text{fus}}S_{\text{MP}}}{R}$$

Again, we are using the subscript MP to indicate that these ΔH and ΔS values are for the melting-point temperature. If, however, the changes in enthalpy and entropy do not change much with temperature, we can approximate $\Delta_{\text{fus}}H \approx \Delta_{\text{fus}}H_{\text{MP}}$ and $\Delta_{\text{fus}}S \approx \Delta_{\text{fus}}S_{\text{MP}}$. We substitute to eliminate $\Delta_{\text{fus}}H_{\text{MP}}$ and $\Delta_{\text{fus}}S_{\text{MP}}$.

$$\ln x_{\text{dissolved solute}} = -\frac{\Delta_{\text{fus}}H}{RT} + \frac{\Delta_{\text{fus}}S}{R} + \frac{\Delta_{\text{fus}}H}{RT_{\text{MP}}} - \frac{\Delta_{\text{fus}}S}{R}$$

Then, we note that the two terms in $\Delta_{\text{fus}}S$ cancel. The two terms in $\Delta_{\text{fus}}H$ can be combined and factored; the final equation is

$$\ln x_{\text{dissolved solute}} = -\frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{MP}}}\right) \qquad \textbf{(7.39)}$$

This is the basic equation for calculating solubilities of solids in solutions. As usual, all temperatures must be in units of absolute temperature. Note that the solubility is given in terms of the mole fraction of the dissolved solute in the solution. If a solubility in terms of molarity or grams per liter is desired, the appropriate conversions must be applied.

Example 7.10

Calculate the solubility of solid naphthalene, $C_{10}H_8$, in liquid toluene, $C_6H_5CH_3$, at 25.0°C if the heat of fusion of naphthalene is 19.123 kJ/mol and its melting point is 78.2°C.

Solution

Using equation 7.39, we get

$$\ln x_{\text{dissolved solute}} = -\frac{19.123\ \frac{\text{kJ}}{\text{mol}}}{0.008314\ \frac{\text{kJ}}{\text{mol·K}}}\left(\frac{1}{298.15\ \text{K}} - \frac{1}{351.35\ \text{K}}\right)$$

Notice that we have converted the value for R into kJ units, and also the temperature values into absolute temperature. All of the units cancel algebraically, as they should. We get

$$\ln x_{\text{dissolved solute}} = -2300.1(0.0033542 - 0.0028461)$$

$$\ln x_{\text{dissolved solute}} = -1.1687$$

Now we take the inverse natural logarithm:

$$x_{\text{dissolved solute}} = 0.311$$

Experimentally, the mole fraction $x_{\text{dissolved solute}}$ is 0.294 for naphthalene dissolved in toluene. Note the good agreement between the calculated and experimental values, especially considering the assumptions made in deriving equation 7.39.

Example 7.11

Use equation 7.39 to justify the effect on solubility for a compound if the temperature is increased. Assume that the temperature is lower than the melting point of the pure solute.

Solution

If $\Delta_{\text{fus}}H$ is positive (and by definition, it is), then the term $-(\Delta_{\text{fus}}H)/R$ is negative. When the temperature is increased, $1/T$ gets smaller, so the value of $[(1/T - (1/T_{\text{MP}})]$ gets smaller. (When $T < T_{\text{MP}}$, $1/T > 1/T_{\text{MP}}$. So as $1/T$ gets smaller, the difference $[(1/T) - (1/T_{\text{MP}})]$ gets smaller.) Therefore, the product $[-(\Delta_{\text{fus}}H)/R][1/T) - (1/T_{\text{MP}})]$ becomes a smaller negative number as T increases. The inverse logarithm of a smaller negative number is a larger decimal number. So, as T increases, $x_{\text{dissolved solute}}$ increases. In other words, as the temperature is increased, the solubility of the solute increases. This is consistent with almost all solutes. (There are a few solutes that decrease in solubility with increase in temperature, but they are rare.)

7.7 Solid/Solid Solutions

Many solids are actually solutions of two or more solid components. Alloys are solid solutions. *Steel* is an alloy of iron, and there are many kinds of steel whose properties depend on the other components of the solution as well as their mole fraction, as shown in Table 7.2. *Amalgams* are alloys of mercury. Many dental fillings are amalgams, which are alloys of mercury (although the perceived danger—not the actual danger!—of mercury poisoning is making amalgam fillings less popular). Bronze (an alloy of copper and tin), brass (an alloy of copper and zinc), solder, pewter, colored glass, doped silicon for semiconductors—are all examples of solid solution.

Table 7.2 Examples of solid/solid solutions[a]

Name	Composition	Uses
Alnico[b]	12 Al, ~20 Ni, 5 Co, remainder Fe	Permanent magnets
Monimax	47 Ni, 3 Mo, remainder Fe	Wire for electromagnets
Wood's metal	50 Bi, 25 Pb, 12.5 Sn, 12.5 Cd	Fire sprinkler systems
Solder	25 Pb, 25 Sn, 50 Bi	Low-melting solder
Stainless steel #304	18–20 Cr, 8–12 Ni, 1 Si, 2 Mn, 0.08 C, rest Fe	A standard stainless steel
Stainless steel #440[c]	16–18 Cr, 1 Mn, 1 Si, 0.6–0.75 C, 0.75 Mo, rest Fe	High-quality stainless steel
Babbitt metal	89 Sn, 7 Sb, 4 Cu	Bearing friction reduction
Constantan	45 Ni, 55 Cu	Thermocouples
Gunmetal	90 Cu, 10 Sn	Guns
Sterling silver	92.5 Ag, 7.5 Cu (or other metal)	Durable silver items

[a] All numbers are in weight percent.
[b] There are several different alnico compositions, some of which have other metallic components.
[c] There are dozens of types of stainless steel, each with its own unique properties.

Solid solutions should be distinguished from *composites,* which are materials formed from two or more solid components that never actually dissolve. Recall that a solution is a mixture that has a consistent composition throughout the system. For example, salt water has a consistent composition at a macroscopic level, even though it is composed of H_2O and NaCl. However, plywood does not, since it is easy to see that it is composed of layers of different material. Composites are not true solid solutions.

For solid/solid solutions, the interesting phase change occurs between possible different solid phases and between solid and liquid phases. In fact, there is a similarity between liquid-gas phase changes and solid-liquid phase changes, which is that the compositions of the phases in a system at equilibrium are not necessarily the same. For solid/solid solutions, the composition of a liquid phase in equilibrium with a solution is a point that must be considered.

The following example shows that the Gibbs phase rule holds for solid solutions as well.

Example 7.12

For a temperature-composition phase diagram of a two-component solid solution, how many degrees of freedom are necessary to describe the system in the following cases?

a. The system is completely solid.

b. There is an equilibrium between solid and liquid phases.

In each case, suggest what variables the degrees of freedom might be.

Solution

a. Using the Gibbs phase rule, for a one-phase solid solution we would have

$$F = C - P + 2 = 2 - 1 + 2$$

$$F = 3$$

The degrees of freedom might be pressure, temperature, and mole fraction of one component. (The other mole fraction is determined by subtraction.)

b. For the case of a solid in equilibrium with a liquid phase, we have

$$F = C - P + 2 = 2 - 2 + 2$$

$$F = 2$$

In this case, we might specify temperature and mole fraction of one component. Since we know that there are two phases in equilibrium, the pressure is dictated by the phase diagram and the equilibrium line between solid and liquid phases at a particular composition and temperature.

An understanding of temperature-composition phase diagrams for solid-liquid phase changes (the most common type) of solid solutions includes an issue brought up in the last section. When a liquid solution reaches a temperature at which solidification occurs, usually a *pure phase* solidifies from the solution. In doing so, the remaining liquid becomes more concentrated in the *other* component. This sounds like fractional distillation, and suggests that a phase diagram like Figure 7.10 or 7.11 might be applicable to solid-liquid phase changes, also. However, it is a little more complicated than that.

First of all, it should be understood that the addition of any solute lowers the freezing point of any solvent—a topic considered in more detail later. For

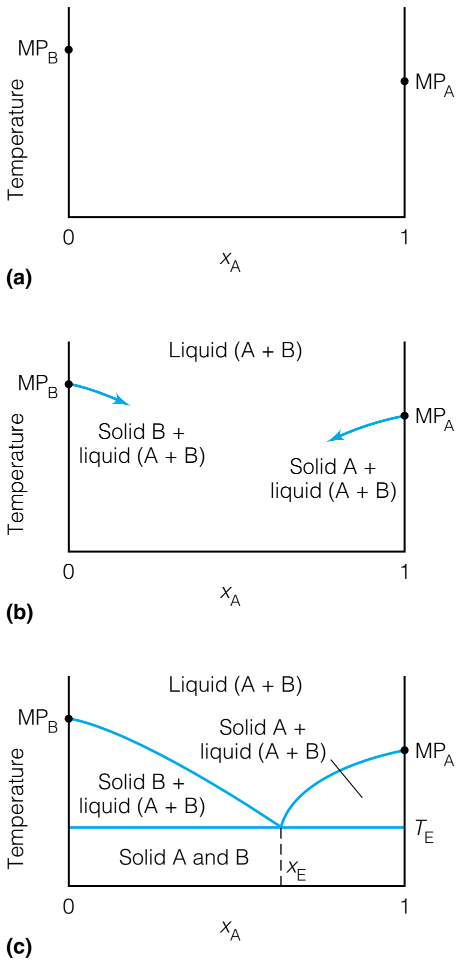

Figure 7.21 Construction of a simple solid-liquid phase diagram for a solid solution. (a) The pure solid components have well-defined melting points. (b) Moving in from either side, as some of the other component is introduced, the melting point drops. Above each line segment, the system is in the liquid state. Below each line segment, there is some liquid and some of the majority component is freezing. (c) At some point, the two lines will meet. Below this point, the system is solid. The phase diagram can thus be divided into areas of all solid, solid + liquid, and liquid. The two "solid + liquid" regions have different compositions, however.

example, we can start with two pure components A and B, which have specific melting points (MPs), as shown in the temperature-composition phase diagram in Figure 7.21a. These mole fractions are represented by $x_A = 1$ and $x_A = 0$, respectively. Starting from each side of the diagram, as each pure component gets impure—that is, as we move from each side toward the middle of the phase diagram—the melting point drops (Figure 7.21b). The phase diagram represents this as a boundary line between a solid phase—either pure B or pure A—in equilibrium with a liquid phase, as marked. As we get more and more impure from either side, eventually the two solid-liquid equilibrium lines will meet, as shown in Figure 7.21c. At this point, both solids A and B will freeze.

Starting from either side of the phase diagram, the situation is very much like a liquid-vapor phase change: one component will preferentially change phase, and the other component will become more and more concentrated within the remaining liquid. Until, that is, a certain composition labeled x_E is reached: then the two components will freeze simultaneously, and the solid that forms will have the same composition as the liquid. This composition is called the *eutectic composition.* At this composition, this liquid acts as if it were a pure component, so the solid and liquid phases have the same composition when in equilibrium at the eutectic temperature T_E. This "pure component" is called the *eutectic.* The eutectic is similar to the azeotrope in liquid-vapor phase diagrams. Not all systems will have eutectics, some systems may have more than one, and the composition of the eutectic(s) of a multicomponent system is characteristic of the components. That is, you cannot predict a eutectic for any given system.

Figure 7.21c therefore shows the behavior of the solid mixture of A and B and how the solid and liquid phases behave with change in temperature. Below the eutectic temperature T_E, the system is a solid. Above the eutectic temperature, it may be either only a liquid phase (if at the eutectic composition), or a combination of pure solid plus a liquid mixture.

Example 7.13

Figure 7.22a shows a phase diagram of two components, A and B. It also shows two initial points, the dots M and N.

a. Explain the behavior of the components as the system starts at point M and cools.

b. Explain the behavior of the components as the system starts at point N and warms.

Solution

a. Point M represents a liquid having mostly component B, since the mole fraction of A is approximately 0.1. As you go down the phase diagram vertically, the two-component liquid drops in temperature until it reaches the solid-liquid equilibrium line. At this point, pure component B solidifies, and the remaining liquid actually gets more concentrated in component A. When it reaches 0.2 mole fraction in A, the eutectic composition is reached and the liquid solidifies as if it were a pure substance, continuing to cool as a eutectic solid of A and B. Figure 7.22b shows a dotted-line path indicating these changes.

b. Point N represents a solid phase having roughly equal parts of A and B. As the temperature increases, eventually a point is reached in which component

A begins to melt. This reduces the amount of A in the solid (indicated by the dotted line above the solid line in Figure 7.22b). When enough A melts that the solid has the eutectic composition, the solid melts evenly as if it were a pure compound. After the solid melts evenly, the system is composed of a single liquid phase.

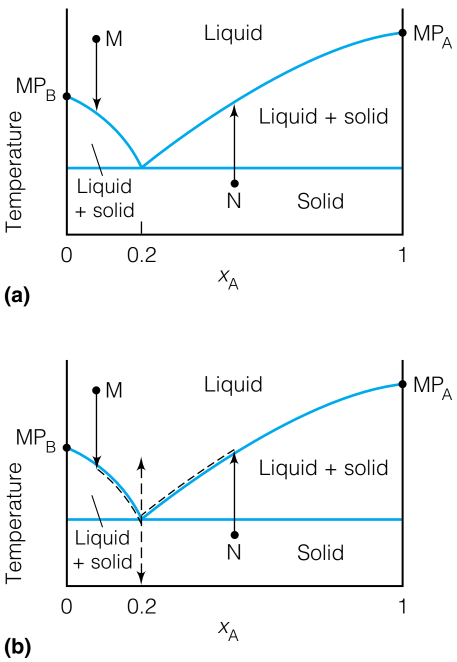

Figure 7.22 The phase diagram described in Example 7.13.

As with azeotropes, eutectics may be ternary, quaternary, and so on, but their phase diagrams get very complex very quickly. A few important eutectics have an impact on ordinary life. Ordinary solder is a eutectic of tin and lead (63% and 37%, respectively) that melts at 183°C, whereas the melting points of tin and lead are 232°C and 207°C. Wood's metal is an alloy of bismuth, lead, tin, and cadmium (50:25:12.5:12.5) that melts at 70°C (lower than the boiling point of water!) that can be used in overhead fire sprinkler systems. NaCl and H_2O make a eutectic that melts at −21°C, which should be of some interest to communities that use salt on icy roads in the winter. (The composition of this eutectic is about 23 weight percent NaCl.) An unusual eutectic exists for cesium and potassium. In a 77:23 ratio, this eutectic melts at −48°C! This eutectic would be a liquid metal at most terrestrial temperatures (and be very reactive toward water).

In many cases, the solid-liquid equilibria are much more complicated than Figures 7.21 and 7.22 suggest. This is due to two factors. First, solids may not be "soluble" in all proportions, so there may be regions of immiscibility in the temperature-composition phase diagram. Second, two components may form *stoichiometric compounds* that can act as pure components. For example, in the phase diagram for Na and K solutions, a "compound" having the stoichiometry Na_2K can form. The presence of this stoichiometric compound can further complicate the phase diagram. Figure 7.23 shows this in a temperature-composition phase diagram for a Na/K solid/liquid solution. Other phase diagrams can get much more complicated, as shown in Figure 7.24.

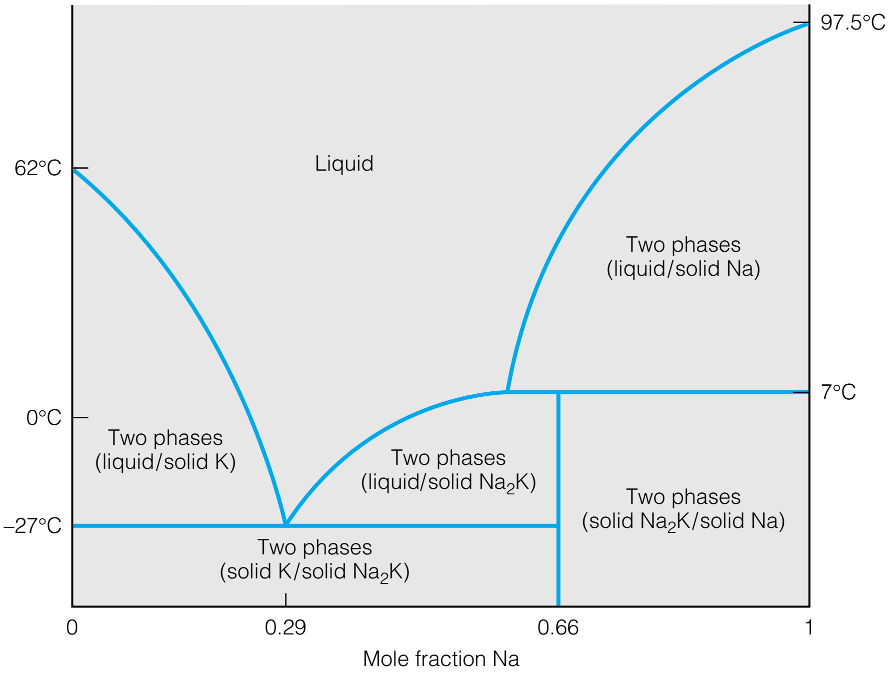

Figure 7.23 A more complicated solid solution phase diagram. This is for the Na/K system. This phase diagram shows the existence of a stoichiometric compound, Na_2K. *Source:* Adapted from T. M. Duncan and J. A. Reimer, *Chemical Engineering Design and Analysis: An Introduction,* Cambridge University Press, 1998.

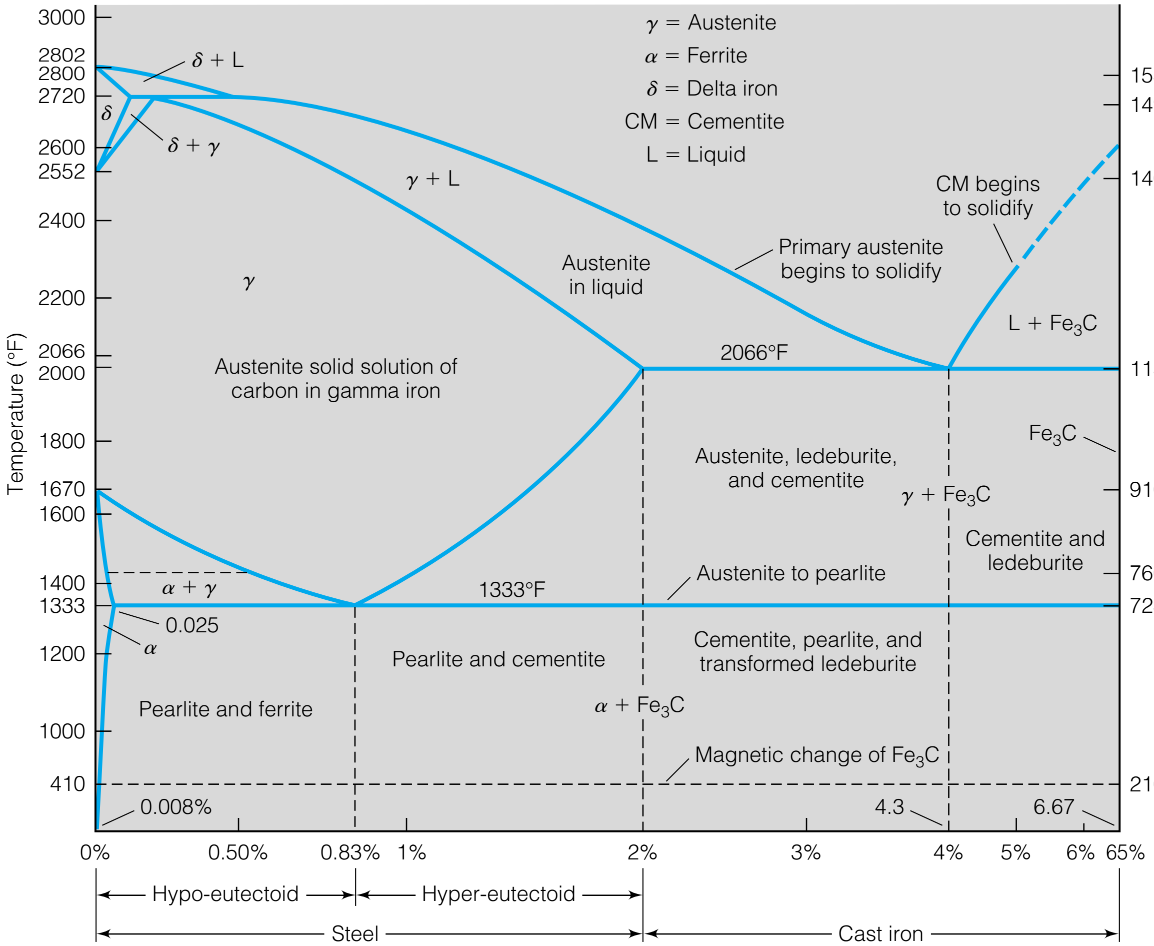

Figure 7.24 A more complicated solid solution phase diagram, in this case describing the system Fe/C.

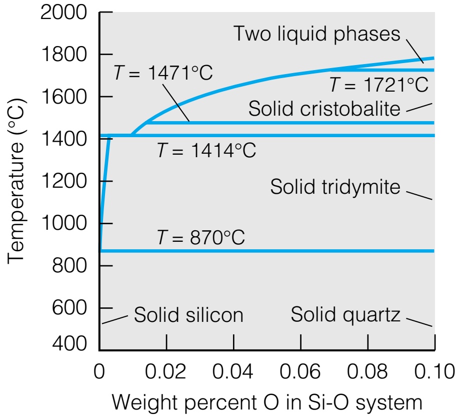

Figure 7.25 The temperature-composition phase diagram for silicon and silicon oxides. This phase diagram is very important to the semiconductor industry, where ultrapure silicon is the first step in making microchips.

One important application of the detailed understanding of solid solution phases is called *zone refining,* which is a method for preparing very pure materials. It is especially useful in the semiconductor industry, where the production of ultrapure silicon is the crucial first step in making semiconductors. Figure 7.25 shows a temperature-composition phase diagram for silicon and silicon oxides. "Pure" silicon, which would have a composition very near the zero value for weight percent of oxygen in Figure 7.25, still has enough impurities to cause problems with the electrical properties of silicon, so it must be purified further.

A solid cylinder of Si, called a *boule,* is slowly passed through a cylindrical high-temperature furnace, as shown in Figure 7.26. (Silicon melts at 1410°C.) When it slowly resolidifies, it does so as very pure silicon, and the impurities remain in the melted phase. As the boule passes further through the furnace, this impure layer collects more of the impurities as the ultrapure silicon crystallizes. In the end, as seen in Figure 7.26, the entire boule has passed through the furnace and the impurities are concentrated in one end, which is cut off. What remains is a cylinder of ultrapure crystalline silicon that can be cut into thousands or millions of semiconductors. Other crystals, including synthetic gemstones, can be fashioned in this way.

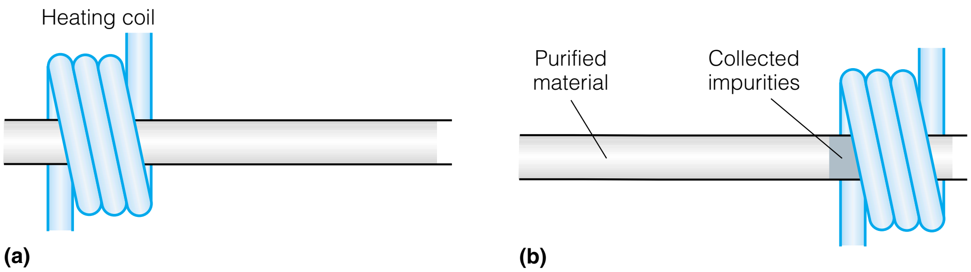

Figure 7.26 In zone refining of silicon, a heating coil melts a small part of the boule at a time. As the liquid slowly solidifies, impurities remain concentrated in the liquid phase. As the molten zone passes along the boule, eventually the impurities are collected at one end, which can then be removed from the pure material.

7.8 Colligative Properties

Consider the solvent of a solution. It is typically defined as the component with the majority mole fraction, although with concentrated aqueous solutions this definition is often relaxed. Compare the properties of a solution with a nonvolatile solute with the same properties of the pure solvent. In certain cases, the physical properties are different. These properties differ because of the presence of solute molecules. The properties are independent of the *identity* of the solute molecules, and the change in the property is related only to the *number* of solute molecules. These properties are called *colligative properties,* where the word *colligative* comes from the Latin words meaning "to bind together" which is what the particles of solute and solvent are doing, in a sense. The four common colligative properties are vapor pressure depression, boiling point elevation, freezing point depression, and osmotic pressure.

We have already addressed vapor pressure depression, in the form of Raoult's law. The vapor pressure of a pure liquid is lowered when a solute is added, and the vapor pressure is proportional to the mole fraction of the solvent:

$$p_{\text{solv}} = x_{\text{solv}} p^{\star}_{\text{solv}}$$

where p_{solv} is the true pressure of the solvent, $p^{\star}_{\text{solv}}$ is the vapor pressure of the pure solvent, and x_{solv} is the mole fraction of the solvent in the solution. Since mole fractions are always 1 or less, the vapor pressure of a solvent in a solution *is always less than the vapor pressure of the pure liquid.* Notice, too, that Raoult's law doesn't care what the solute is, it only depends on the mole fraction of the solvent. This is one of the characteristics of a colligative property. It's not what, but *how much.*

Before considering the next colligative properties, we recall the concentration unit *molality.* The molality of a solution is similar to molarity except that it is defined in terms of the number of kilograms of solvent, not liters of solution:

$$\text{molality} \equiv \frac{\text{number of moles of solute}}{\text{number of kilograms of solvent}} \qquad \textbf{(7.40)}$$

Molality, abbreviated molal or m, is useful for colligative properties because it is a more direct ratio of molecules of solute to molecules of solvent. The unit molarity automatically includes the concept of partial molar volumes because it is defined in terms of liters of *solution,* not liters of solvent. It is also dependent on the amounts of solvent and solute (in mole and kilogram units), but independent of volume or temperature. Thus, as T changes, the concentration in molality units remains constant while the concentration in molarity units varies due to expansion or contraction of the solution's volume.

The next colligative property is *boiling point elevation.* A pure liquid has a well-defined boiling point at a particular pressure. If a nonvolatile solute were added, then to some extent those solute molecules would impede the ability of solvent molecules to escape from the liquid phase, so more energy is required to make the liquid boil, and the boiling point increases.

Similarly, nonvolatile solvents will make it harder for solvent molecules to crystallize at their normal melting points because solidification will be impeded. Therefore, a lower temperature will be required to freeze the pure solvent. This defines the idea of *freezing point depression.* A pure liquid will have its freezing point lowered when a solute is dissolved in it. (This idea is a common one for anyone who has tried to synthesize a compound in a lab. An impure compound will melt at a lower temperature because of the freezing point depression of the "solvent.")

Because the liquid-gas and liquid-solid transitions are equilibria, we can apply some of the mathematics of equilibrium processes to the changes in phase transition temperatures. In both cases the argument is the same, but here we will concentrate on the liquid-solid phase equilibrium and then apply the final arguments to the liquid-gas phase change.

In some respects, the freezing point depression can be considered in terms of solubility limits, which we discussed in the previous section. This time, instead of the component of interest being the solute, the component of interest is the *solvent.* However, the same arguments and equations apply. By analogy, we can adapt equation 7.39 and say that

$$\ln x_{\text{solvent}} = -\frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{MP}}}\right) \tag{7.41}$$

where $\Delta_{\text{fus}}H$ and T_{MP} refer to the heat of fusion and melting point of the solvent. If we are considering dilute solutions, then x_{solvent} is very close to 1. Since $x_{\text{solvent}} = 1 - x_{\text{solute}}$, we can substitute to get

$$\ln(1 - x_{\text{solute}}) = -\frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{MP}}}\right) \tag{7.42}$$

Using a one-term Taylor series expansion of $\ln(1 - x) \approx -x$,* we substitute for the logarithm on the left side of the equation and get

$$x_{\text{solute}} \approx \frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{MP}}}\right) \tag{7.43}$$

where the minus signs have canceled. This equation is rewritten by algebraically rearranging the temperature terms:

$$x_{\text{solute}} \approx \frac{\Delta_{\text{fus}}H}{R}\,\frac{T_{\text{MP}} - T}{T \cdot T_{\text{MP}}} \tag{7.44}$$

We make one last approximation. Since we are working with dilute solutions, the temperature of the equilibrium is not much different from the normal melting point temperature T_{MP}. (Recall that the freezing point and the melting point are the same temperature and that the phrases "freezing point" and "melting point" can be used interchangeably.) Therefore, we substitute T_{MP} for T in the denominator of equation 7.44, and define ΔT_{f} as $T_{\text{MP}} - T$: the change

---

*The multiterm expansion is $\ln(1 - x) = -x - \frac{1}{2}x^2 - \frac{1}{3}x^3 - \frac{1}{4}x^4 - \cdots$.

in temperature of the equilibrium melting or freezing process. Equation 7.44 becomes

$$x_{\text{solute}} \approx \frac{\Delta_{\text{fus}}H}{RT_{\text{MP}}^2}\Delta T_{\text{f}} \tag{7.45}$$

The relationship between molality and mole fraction is simple. If M_{solvent} is the molecular weight of the solvent, then the molality of the solution is

$$m_{\text{solute}} = \frac{1000 \cdot x_{\text{solute}}}{x_{\text{solvent}} \cdot M_{\text{solvent}}} \tag{7.46}$$

The 1000 in the numerator of equation 7.46 represents a conversion from grams to kilograms, so there is an implicit g/kg unit on it. Remember that the mole fraction of the solvent is close to 1, so we further approximate by substituting 1 for x_{solvent}. We then rearrange equation 7.46 in terms of x_{solute}, substitute into equation 7.45, and then rearrange the equation to get an expression for ΔT_{f}, the amount that the freezing point is depressed. We get

$$\Delta T_{\text{f}} \approx \left(\frac{M_{\text{solvent}} \cdot RT_{\text{MP}}^2}{1000 \cdot \Delta_{\text{fus}}H}\right)m_{\text{solute}} \tag{7.47}$$

All of the terms relating to properties of the solvent have been grouped inside parentheses, and the only term relating to the solute is its molal concentration. Notice that all of the terms inside the parentheses are a constant for any particular solvent: its molecular weight M_{solvent}, its melting point T_{MP}, and its heat of fusion $\Delta_{\text{fus}}H$. (1000 and R are also constants.) Therefore, this collection of constants represents a constant value for any solvent. Equation 7.47 is more commonly written as

$$\Delta T_{\text{f}} \approx K_{\text{f}} \cdot m_{\text{solute}} \tag{7.48}$$

where K_{f} is called the *freezing point depression constant* for the solvent. It is also called the *cryoscopic constant* for the solvent.

Example 7.14

Calculate the cryoscopic constant for cyclohexane, C_6H_{12}, given that its heat of fusion is 2630 J/mol and its melting point is 6.6°C. What are the units for the constant?

Solution

The molecular weight of cyclohexane is 84.16 g/mol. The melting point, which must be expressed in absolute temperature, is 6.6 + 273.15 = 279.8 K. Comparing equations 7.47 and 7.48, we see that the expression for K_{f} is

$$K_{\text{f}} = \frac{M_{\text{solvent}}RT_{\text{MP}}^2}{1000\ \Delta_{\text{fus}}H}$$

Substituting for the variables:

$$K_{\text{f}} = \frac{(84.16\ \frac{\text{g}}{\text{mol}})(8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}})(279.8\ \text{K})^2}{1000\ \frac{\text{g}}{\text{kg}} \cdot 2630\ \frac{\text{J}}{\text{mol}}}$$

Working out the units, everything cancels but K·kg/mol

$$K_{\text{f}} = 20.83\ \frac{\text{K}\cdot\text{kg}}{\text{mol}}$$

These units seem unusual until one remembers that the unit molality is defined in terms of mol/kg. Since the above unit has the reciprocal of this expression, this implies that the unit molality can be substituted in the denominator. Therefore, the final answer is

$$K_f = 20.83\ \frac{\text{K}}{\text{molal}}$$

This unit makes more sense if one is using equation 7.48 to determine the freezing point depression. Cyclohexane has one of the larger K_f values for a common solvent.

There is an analogous derivation for the difference in the boiling point for a solvent that has a nonvolatile solute dissolved in it. Rather than repeat the derivation in its entirety, only the final result is presented:

$$\Delta T_b \approx \left(\frac{M_{\text{solvent}} \cdot RT_{\text{BP}}^2}{1000\ \Delta_{\text{vap}}H}\right) m_{\text{solute}} \qquad \textbf{(7.49)}$$

where T_{BP} and $\Delta_{\text{vap}}H$ now refer to the boiling point and heat of vaporization of the solvent. Again, the terms inside the parentheses are constants for any solvent, so equation 7.49 can be rewritten as

$$\Delta T_b \approx K_b \cdot m_{\text{solute}} \qquad \textbf{(7.50)}$$

where K_b is the *boiling point elevation constant* for the solvent. It is sometimes called the *ebullioscopic constant.*

One thing that the expressions for the change in the freezing point and boiling point do not address: the *direction* of the change. Although the formal mathematics indicate the direction of ΔT_f and ΔT_b, they are lost in equations 7.48 and 7.50. That is, they tell us only the magnitude of the change, not the direction. It is incumbent on us to remember: freezing points go down, but boiling points go up.

The final colligative property of solutions we will consider is called osmotic pressure. Although we treat it last, it is probably one of the most important, because many biological systems like our own cells are influenced by it.

Pressure is defined as force per unit area. Pounds per square inch (psi) is a common (though non-SI) unit of pressure in the United States. A pressure is exerted on any object that has liquid above it, as experienced divers know. The first barometers invented were tubes of water—and later mercury—that were set up to act against the pressure of the atmosphere. See Figure 7.27.

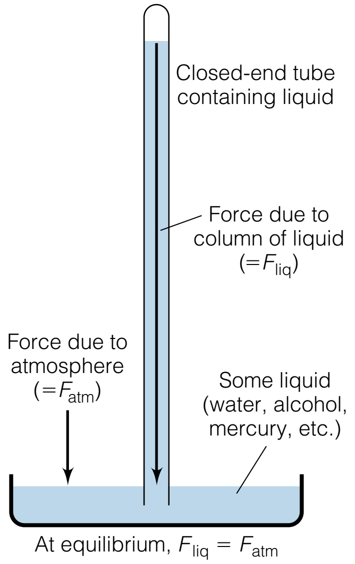

Figure 7.27 An illustration of how opposing pressures act against each other. In this example, the opposing pressures are the pressure of the atmosphere and the pressure of the liquid column in the long tube. At equilibrium, the two pressures balance each other. (This diagram represents a simple barometer.)

Consider a system constructed in two parts that are separated by a semipermeable membrane, as shown in Figure 7.28. A *semipermeable membrane* is a thin film that allows some molecules to pass through it and not others. Cellophane and other polymers are examples. Cell walls can be considered semipermeable membranes. Let the system be filled with a solution on the left side, and the pure solvent on the right side, but to the same height (Figure 7.28a). The tube on either side is open to some external pressure, labeled *P*.

Curiously, this system is *not at equilibrium.* In time, solvent (usually water) molecules, which can easily pass through many semipermeable membranes, will go from the right side to the left side, further diluting the solution. In doing so, the heights of the liquids on either side of the membrane change. At some point, the system achieves equilibrium. That is, the chemical potential of the solvent on either side of the membrane is equal:

$$\mu_{\text{solvent},1} = \mu_{\text{solvent},2}$$

At this point, however, the liquid levels on the two sides of the system are different, as shown in Figure 7.28b. The column of liquid on the left side exerts a different pressure than the column on the right side. The difference in the two pressures, represented by the difference in column heights, is called the *osmotic pressure,* which is given the symbol Π. Therefore, at equilibrium the left side is exerting a total pressure $P + \Pi$ and the right side is now exerting pressure P. Therefore, the equality of the two chemical potentials can be written as

$$\mu(P + \Pi) = \mu^\circ(P) \tag{7.51}$$

where a capital P is used to differentiate this variable from the lowercase p used for gas pressure. The chemical potential of the solution that has a mole fraction of solute, x_{solute}, is related to the standard chemical potential as given by equation 7.35, but in slightly different notation:

$$\mu(P + \Pi) = \mu^\circ(P + \Pi) + RT \ln x_{\text{solute}} \tag{7.52}$$

To determine an expression for Π, we begin with the natural variable expression for $d\mu$:

$$d\mu = -\overline{S}\, dT + \overline{V}\, dp$$

At constant temperature:

$$d\mu = \overline{V}\, dp$$

To find μ, we integrate both sides of the equation from one pressure extreme to the other. In this case, the pressure extremes are P and $P + \Pi$. We get

$$\int_{P}^{P+\Pi} d\mu = \int_{P}^{P+\Pi} \overline{V}\, dp$$

If we actually perform the integration on the left side of this expression, we get

$$\mu_{\text{solvent,solution}}(P + \Pi) - \mu^\circ_{\text{solvent,pure}}(P) = \int_{P}^{P+\Pi} \overline{V}\, dp \tag{7.53}$$

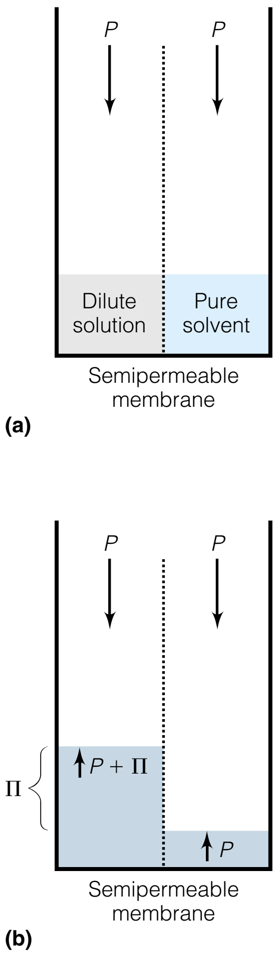

Figure 7.28 The two-part system is filled with pure solvent on one side and a dilute solution on the other. (a) Initially, the liquid levels are even with each other. However, it is not at equilibrium. Solvent will pass through the semipermeable membrane in a preferential direction. (b) At equilibrium, the two levels are uneven. The difference between the two levels is defined as the osmotic pressure Π.

We have embellished the μ's with subscripts: the side where the total liquid pressure is $P + \Pi$ has the solvent combined with a solute, whereas the side where the total liquid pressure is P has the pure solvent (hence the superscript °). Using equation 7.52 to substitute for $\mu(P + \Pi)$ in equation 7.51:

$$\mu^\circ(P + \Pi) + RT \ln x_{\text{solute}} = \mu^\circ(P)$$

Next, rearrange:

$$\mu^\circ(P + \Pi) - \mu^\circ(P) = -RT \ln x_{\text{solute}}$$

The left side of this equation is the same as the left side of equation 7.53 (but without the subscripts). We can substitute and get:

$$-RT \ln x_{\text{solvent,solution}} = \int_{P}^{P+\Pi} \overline{V}\, dp \tag{7.54}$$

If we assume that the molar volume remains constant between pure solvent and solution, $\overline{V}$ can be removed from the integral and the answer is straightforward:

$$\begin{aligned} -RT \ln x_{\text{solvent,solution}} &= \overline{V} \int_{P}^{P+\Pi} dp \\ &= \overline{V} \cdot p\Big|_{P}^{P+\Pi} \\ &= \overline{V}\,(P + \Pi - P) \\ -RT \ln x_{\text{solvent,solution}} &= \overline{V} \cdot \Pi \end{aligned} \tag{7.55}$$

Again, consider that $\ln x_{\text{solvent,solution}} = \ln(1 - x_{\text{solute}}) \approx -x_{\text{solute}}$. Making one final substitution:

$$x_{\text{solute}}RT = \overline{V} \cdot \Pi$$

This is usually rearranged to read as

$$\Pi\overline{V} = x_{\text{solute}}RT \qquad \textbf{(7.56)}$$

This equation, which is a remarkable parallel to the ideal gas law, is called the *van't Hoff equation,* after Jacobus van't Hoff, a Dutch physical chemist who announced this equation in 1886.* (He was also one of the originators of the concept of the tetrahedral carbon atom, and was the first recipient of the Nobel Prize for Chemistry in 1901.) The equation relates the osmotic pressure of a solution to the mole fraction of the solute in the solution. It is strictly valid only for very dilute solutions (reminiscent of many ideal gas systems), but is also a useful guide for more concentrated ones.

Example 7.15

What is the osmotic pressure of a 0.010-molal solution of sucrose in water? If this solution were placed in a system as illustrated in Figure 7.28, how high would the column of diluted sucrose be at equilibrium if the tube has a surface area of 100.0 cm^2? Assume 25°C, and that the density of the solution is 1.01 g/mL. Some necessary conversions are 1 bar = 10^5 pascal, and 1 pascal = 1 N/m^2 (newton of force per square meter of area), and remember that $F = ma$ for converting a mass into its equivalent force. (In this case, a will be the acceleration due to gravity, which is 9.81 m/s^2.)

Solution

A 0.010-molal solution contains 0.010 mole of sucrose in 1.00 kg, or 1000 g, of water. In 1.00 kg of H_2O, there are 1000 g/(18.01 g/mol) = 55.5 mol H_2O. Therefore, the mole fraction of sucrose is

$$\frac{0.010}{55.5 + 0.010} = 0.000180 = x_{\text{solute}}$$

The molar volume of water is 18.01 mL, or 0.01801 L. Using the van't Hoff equation:

$$\Pi(0.01801 \text{ L}) = 0.000180\left(0.08314 \frac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}}\right)298 \text{ K}$$

$$\Pi = 0.248 \text{ bar}$$

This is a substantial osmotic pressure for such a dilute solution! In order to know how high the column will be, we convert this into N/m^2:

$$0.248 \text{ bar} \times \frac{10^5 \text{ pascals}}{1 \text{ bar}} \times \frac{1 \text{ N/m}^2}{1 \text{ pascal}} = 2.48 \times 10^4 \text{ N/m}^2$$

For a surface area of 100.0 cm^2 = 1.00×10^{-2} m^2, this pressure is caused by a force determined as

$$2.48 \times 10^4 \frac{\text{N}}{\text{m}^2} \times 1.00 \times 10^{-2} \text{ m}^2 = 248 \text{ N}$$

---

*This is different from the van't Hoff equation introduced in Chapter 5.

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Figure 7.29 The osmotic pressure of a 0.010-molal solution will support a 100-cm^2 column of solution that is about the height of a baby giraffe!

Using the equation $F = ma$, this force corresponds to a mass of

$$248 \text{ N} = m \cdot 9.81 \frac{\text{m}}{\text{s}^2}$$

$$m = 25.3 \text{ kg}$$

where we have used the fact that 1 N = 1 kg·m/s^2. At a density of 1.01 g/mL, this is

$$25.3 \text{ kg} \cdot \frac{1000 \text{ g}}{1 \text{ kg}} \cdot \frac{1 \text{ mL}}{1.01 \text{ g}} \cdot \frac{1 \text{ cm}^3}{1 \text{ mL}} = 2.50 \times 10^4 \text{ cm}^3$$

where we have used the equality 1 cm^3 = 1 mL in the last step. For an area of 100.0 cm^2, this corresponds to a column having a height of

$$\frac{2.50 \times 10^4 \text{ cm}^3}{100.0 \text{ cm}^2} = 250. \text{ cm}$$

That's almost 8 feet high! Figure 7.29 gives you an idea how high this is.

Although 0.010 molal is not a very concentrated solution, the predicted osmotic pressure effects are substantial.

Osmotic pressure considerations have some important applications. One is in biology. A cell membrane is a semipermeable membrane. Therefore, osmotic pressures on either side of the membrane must be very close to equal, or the effects of osmotic pressure may cause cells to either collapse or expand due to transfer of H_2O from regions of low concentrations to high concentrations. Either expansion or collapse can kill the cell. Figure 7.30 shows photographs of red blood cells in solutions of higher, equal, and lower osmotic pressures. Osmotic pressure effects also explain why people stranded in lifeboats on the ocean cannot safely drink the seawater. Its osmotic pressure is too high, and drinking it will cause one's cells to literally dehydrate, rather than hydrate.

Osmotic pressure is also a factor in delivering water from the roots of trees to the leaves in their tops, which might be dozens or even hundreds of feet from the ground. It is also important in keeping nonwoody plants sturdy and upright, and uncooked vegetables crisp and crunchy.

Osmotic pressure can be used to determine the average molecular weights of macromolecules and polymers. As Example 7.15 showed, significant osmotic pressure effects do not require a large concentration. Relatively dilute solutions can show measurable osmotic effects, which allow one to calculate the molality of the solution and, stepwise, the molecular weight of the solute. Of course, if the high-molecular-weight polymer is even slightly impure, the number of presumably lower-molecular-weight impurities will dramatically affect the final determination. Again, this is because osmotic pressure is a colligative property, which depends only on the number of molecules, not their identities, in the solution.

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Figure 7.30 Demonstration of the effects of osmotic pressure on red blood cells. If the osmotic pressures inside and outside the cell are equal, the cells look normal. However, if the osmotic pressure outside the cell is too low, the cells swell; if it is too high, the cells shrivel. Neither situation is good for the body.

Example 7.16

An aqueous poly(vinyl alcohol) solution that is made by dissolving 0.0100 g of polymer in 1.00 L of water has an osmotic pressure of 0.0030 bar. What is the average molecular weight of the polymer? Assume 298 K, and also assume that the volume of the solvent does not change appreciably when the solute is added.

Solution

Using the van't Hoff equation, we set up the following expression:

$$(0.0030\ \text{bar})\overline{V} = x_{\text{solute}}\left(0.08314\ \frac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}}\right)298\ \text{K}$$

We still need $\overline{V}$ and x_{solute}. But since the mole fraction of the solute is so small, we can approximate that

$$\frac{x_{\text{solute}}}{\overline{V}} \approx \frac{n_{\text{solute}}}{V_{\text{solution}}} = \text{molarity of solution}$$

(Notice that we are no longer using the molar volume, $\overline{V}$.) We can therefore determine the molarity of the solution by rearranging the equation to

$$\text{molarity} \approx \frac{n_{\text{solute}}}{V} = \frac{0.0030\ \text{bar}}{(0.08314\ \frac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}})\,298\ \text{K}}$$

Working out the numbers and the units, we find that

$$\text{molarity} \approx 0.000123\ \frac{\text{mol}}{\text{L}}$$

Using the fact that 0.0100 g was used to make 1.00 L of solution, we have the relationship

$$0.000123\ \frac{\text{mol}}{\text{L}} = 0.0100\ \frac{\text{g}}{\text{L}}$$

The liter units cancel, giving

$$0.000123\ \text{mol} = 0.0100\ \text{g}$$

Solving for molecular weight, which has units of g/mol, we find that the molecular weight is

$$815{,}000\ \frac{\text{g}}{\text{mol}}$$

This is not an unusual average molecular weight for a polymer.

The osmotic pressure of a solution can be counteracted by exerting additional pressure on the side of the membrane that has the more concentrated solution. In fact, if p_{ext} is greater than Π, then the osmosis process will occur *in the opposite direction.* Such "reverse osmosts" processes have some extremely practical benefits. Perhaps the most important is the production of fresh water from seawater in desalinization plants. In the Middle East, these plants produce drinkable water from the very salty water of the gulfs and seas in the area. The process is a product of technology, but is much less energy-intensive than distillation.

The van't Hoff equation assumes that the solute dissolves molecularly. That is, every molecule of solid solute dissolves into a single molecule of solute in a solvated form. For compounds that dissolve into multiple solvated species (mainly ionic compounds), the number of species that the solute dissolves into must be taken into account. For such compounds, the van't Hoff equation becomes

$$\Pi \overline{V} = N \cdot x_{\text{solute}} RT \qquad \textbf{(7.57)}$$

where N represents the number of individual species a compound separates into when it dissolves.

7.9 Summary

Solutions, even binary solutions, can be complicated in their behavior. The equations of thermodynamics help us understand this behavior. Liquid/liquid solutions can establish equilibria with vapor phases, and the equations of thermodynamics help us understand how the composition of the vapor phase is related to the composition of the liquid phase. We can do the same thing for solid/solid solutions and the liquid phase that will exist when such a solution melts. Both phase changes have a special composition that acts as a pure phase: an azeotrope or a eutectic. Both special compositions affect our everyday life.

Phase diagrams are useful graphical representations of the phase changes and compositions of solutions. Not only do they represent instantaneous conditions, but they can be used to predict the behavior of a solution as conditions change. Properly labeled and interpreted, a phase diagram indicates the exact composition of the different phases that appear as conditions like temperature or pressure change. Phase diagrams for real solutions show how azeotropes and eutectics can't be avoided.

Colligative properties address the changes in the physical properties of the solution with respect to the major component—the solvent. Raoult's law summarizes the change in the vapor pressure of a volatile solvent. Freezing points and boiling points change. But osmotic pressure may be the most underrated colligative property. It is a factor in biological cells and our ability to make fresh water from seawater. Luckily, the equations of thermodynamics provide an understanding of all of these phenomena.

EXERCISES FOR CHAPTER 7

7.2 The Gibbs Phase Rule

7.1. Consult Example 7.1 and assume that now your mixed drink has an olive in it. Now how many degrees of freedom are there? What might you select as the variables to be specified?

7.2. Referring to Example 7.2, how many degrees of freedom are specified when there is only $Fe_2(SO_4)_3$ in the system?

7.3. How many phases are necessary in a three-component system if you want no degrees of freedom?

7.4. Can there ever be a negative number of degrees of freedom for any possible one-component physical system at equilibrium?

7.5. For the following chemical equilibrium in an enclosed system, how many degrees of freedom are there?

$$2NaHCO_3\ (s) \overset{\text{high } T}{\rightleftharpoons} Na_2CO_3\ (s) + H_2O\ (\ell) + CO_2\ (g)$$

7.6. The production of nitrogen gas for automobile airbags takes advantage of the following chemical reaction:

$$4NaN_3\ (s) + O_2\ (g) \longrightarrow 6N_2\ (g) + 2Na_2O\ (s)$$

If this reaction were in equilibrium, how many degrees of freedom would be necessary to describe the system?

7.3 Liquid/Liquid Systems

7.7. Assuming that the vapors act like an ideal gas, what is the minimum amount of H_2O needed in a 5.00-L system at 25.0°C to ensure that there is a liquid phase in equilibrium with a vapor phase? What is the minimum amount of CH_3OH needed to ensure a liquid phase and vapor phase under the same conditions? The equilibrium vapor pressures of H_2O and CH_3OH at this temperature are 23.76 and 125.0 torr, respectively.

7.8. For a solution of H_2O and CH_3OH in which $x_{H_2O} = 0.35$, what are the mole fractions of H_2O and CH_3OH in the vapor phase? Use conditions and data from exercise 7.7.

7.9. What is the activity of liquid H_2O of a multicomponent solution in which the vapor pressure of H_2O is 748.2 mmHg at 100.0°C?

7.10. Derive equation 7.19.

7.11. Derive equation 7.19 but in terms of y_2, not y_1.

7.12. Determine the total equilibrium pressure of the vapor in equilibrium with a 1:1 molar ratio of hexane (C_6H_{14}) and cyclohexane (C_6H_{12}) if the equilibrium vapor pressures of the two components are 151.4 and 97.6 torr, respectively.

7.13. Many police departments use breath tests to check for drunk drivers. What would be the approximate partial pressure of ethanol in expired breath if the blood alcohol content is approximately 0.06 mole % (that is, $x_{\text{ethanol}} = 0.0006$)? The equilibrium vapor pressure of C_2H_5OH at 37°C is 115.5 torr. Use your answer to comment on the necessary sensitivity of the test.

7.14. A solution of methanol (CH_3OH) and ethanol (C_2H_5OH) has a vapor pressure of 350.0 mmHg at 50.0°C. If the equilibrium vapor pressures of methanol and ethanol were 413.5 and 221.6 mmHg, respectively, what is the composition of the solution?

7.15. Derive equation 7.23 from equation 7.19.

7.16. Determine the mole fractions of each component in the vapor phase of the vapor in equilibrium with a 1:1 molar ratio of hexane (C_6H_{14}) and cyclohexane (C_6H_{12}) if the equilibrium vapor pressures of the two components are 151.4 and 97.6 torr, respectively.

7.17. Use equation 7.24 to show that $\lim_{y_1=0} p_{\text{tot}} = p_2^*$ and $\lim_{y_2=0} p_{\text{tot}} = p_1^*$.

7.18. Why could one not use equation 7.24 directly to determine the total pressure of the vapor in Example 7.5?

7.19. What are $\Delta_{\text{mix}}G$ and $\Delta_{\text{mix}}S$ for the combination of 1.00 mol of toluene and 1.00 mol of benzene at 20.0°C? Assume that they mix to make an ideal solution.

7.4 Nonideal Liquid/Liquid Systems

7.20. Why is acetone used to rinse out wet glassware? (*Hint:* Water has a boiling point of 100.0°C and acetone has a boiling point of 56.2°C. There is also a low-boiling azeotrope composed of the two molecules.)

7.21. Repeat Example 7.7, but assume that you start with a solution that has $x_1 = 0.1$ using Figure 7.14 as the phase diagram.

7.22. Repeat Example 7.7, but assume that you start with a solution that has $x_1 = 0.4$ using Figure 7.15 as the phase diagram.

7.23. How might you be able to distinguish an azeotrope from a pure compound by purely physical means? (*Hint:* consider other possible phase changes.)

7.24. Ethanol prepared by distillation is only about 95% pure because it forms a low-boiling binary azeotrope with water. "100%" ethanol can be made by adding a specific amount of benzene to form a ternary azeotrope that boils at 64.9°C. However, this ethanol should not be ingested! Why?

7.25. Figure 7.31 shows a phase diagram of H_2O and ethylene glycol. Explain why this mixture, in an approximately 50:50 mixture, is used as a coolant and antifreeze in automobile engines.

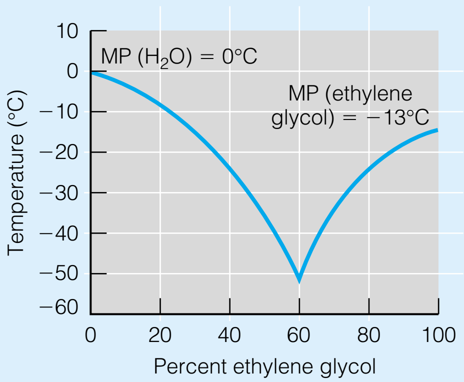


Figure 7.31 A temperature-composition phase diagram of water and ethylene glycol. Refer to exercise 7.25.

7.5 Liquid/Gas Systems and Henry's Law

7.26. Convert the units of the Henry's law constant for CO_2, in Table 7.1, to units of mmHg, atm, and bar. In which case(s) does the numerical value of the constant change?

7.27. What is the difference between hydrogen chloride and hydrochloric acid? Do you expect that either of them acts as an ideal substance?

7.28. The Henry's law constant for methyl chloride, CH_3Cl, in aqueous solution is 2.40×10^6 Pa. What pressure of methyl chloride is necessary to establish a mole fraction of 0.0010 in an aqueous solution?

7.29. The mole fraction of CCl_2F_2, a compound once used as a refrigerant, in an aqueous solution was found to be 4.17×10^{-5} at normal pressure. What is the approximate molarity of this solution and what is the Henry's law constant for this gas? Use a density of 1.00 g/cm^3 for water.

7.30. At 25°C, the mole fraction of air in water is about 1.388×10^{-5}. **(a)** What is the molarity of this solution? **(b)** What is the Henry's law constant for air? **(c)** Would you expect the solubility of air to increase or decrease with an increase in temperature? Compare your numerical answers to the constants for nitrogen and oxygen in Table 7.1.

7.31. At 25°C, the mole fraction of nitrogen, N_2 (g), in water is 1.274×10^{-5}. **(a)** Compare this with the number in the previous problem and comment. **(b)** Calculate the solubility of oxygen, O_2 (g), in water given the fact that air is approximately 80% nitrogen and 20% oxygen. **(c)** Calculate the Henry's law constant for oxygen. Compare your answer to the number in Table 7.1.

7.32. Does a higher Henry's law constant mean that a gas is more soluble in a liquid, or less soluble? Be able to defend your answer.

7.6 & 7.7 Liquid/Solid and Solid/Solid Solutions

7.33. What is the approximate molarity of a saturated solution of phenol, C_6H_5OH, for which 87.0 g can be dissolved in 100 mL of water? The density of phenol is 1.06 g/cm^3; assume ideal behavior with respect to the total volume of the solution.

7.34. Calculate the solubility of phenol, C_6H_5OH, in water at 25°C if $\Delta_{fus}H$ for phenol is 11.29 kJ/mol and its melting point is 40.9°C. Compare the calculated solubility with the numbers from the previous exercise. Can you explain any deviations?

7.35. (a) Convert the calculated mole fraction of naphthalene dissolved in toluene from Example 7.10 into molarity, assuming that the volumes are strictly additive. The density of toluene is 0.866 g/mL and the density of naphthalene is 1.025 g/mL. Assume the volumes are additive.

(b) Estimate the solubility, in g/100 mL and molarity, of naphthalene in *n*-decane, $C_{10}H_{22}$, which has a density of 0.730 g/mL.

7.36. Will equation 7.39 work for the solubility of gases in liquids? Why or why not?

7.37. Consider the following solutions:

Sodium chloride (s) in water
Sucrose (s) in water
$C_{20}H_{42}$ (s) in cyclohexane
Water in carbon tetrachloride

For which solution(s) do you think that a calculated solubility will be close to the experimental solubility? Explain your reasoning.

7.38. Determine how ideal the following solutions are by calculating the mole fraction of solute in each solution, and comparing that to the expected mole fractions. All data are for 25.0°C.

(a) 14.09 weight percent of I_2 in C_6H_6, MP of I_2 is 112.9°C (sublimes), and $\Delta_{fus}H$ = 15.27 kJ/mol

(b) 2.72 weight percent of I_2 in C_6H_{12}, MP of I_2 is 112.9°C (sublimes), and $\Delta_{fus}H$ = 15.27 kJ/mol

(c) 20.57 weight percent of *para*-dichlorobenzene, $C_6H_4Cl_2$, in hexane, MP of $C_6H_4Cl_2$ is 52.7°C, and $\Delta_{fus}H$ = 17.15 kJ/mol

7.39. Iron metal has a $\Delta_{fus}H$ value of 14.9 kJ/mol and is soluble in mercury to the level of $x_{Fe} = 8.0 \times 10^{-3}$ at 25.0°C. Estimate the melting point of iron. Compare the estimate to the literature value of 1530°C.

7.40. How many degrees of freedom are required to specify the eutectic for a two-component system?

7.41. Do communities that use salt in the winter use enough to form the low-melting eutectic between NaCl and H_2O, or are they taking advantage of the freezing-point depression phenomenon in general? How can you tell?

7.42. Starting from $x_{Na} = 0.50$ in Figure 7.23 in the liquid region, describe what happens as the temperature is decreased until the entire solution is solid.

7.43. Construct a qualitative phase diagram for the Sn/Sb system, which has binary eutectics at 92% and 95% Sn that melt at 199°C and 240°C, respectively. The melting points of tin and antimony are 231.9°C and 630.5°C.

7.44. Explain why zone refining, used to make ultra-pure silicon, would not be a practical method of making ultra-pure carbon.

7.45. Estimate the solubility of Na in Hg at 0°C. The heat of fusion of sodium is 2.60 kJ/mol and its melting point is 97.8°C.

7.46. Show how the formula of the stoichiometric compound in Figure 7.23 was determined.

7.8 Colligative Properties

7.47. Explain how the unit molarity automatically includes the concept of partial molar volumes.

7.48. Why do you think people who live at high altitudes are advised to add salt to water when boiling food like pasta? What mole fraction of NaCl is needed to raise the boiling point of H_2O by 3°C? Does the amount of salt added to water (typically about one teaspoon to four quarts of water) substantially change the boiling point? K_b (H_2O) = 0.51°C/molal.

7.49. Estimate the osmotic pressure, freezing point, and boiling point of seawater, which you can approximate as equivalent to a 1.08-molal solution of NaCl. Use equations 7.47 and 7.49 to calculate K_f and K_b for H_2O, and use $\Delta_{fus}H\ [H_2O] = 6.009$ kJ/mol and $\Delta_{vap}H\ [H_2O] = 40.66$ kJ/mol. From what you know about seawater, what assumptions are we making?

7.50. Calculate the freezing point depression of mercury caused by dissolved sodium if the mole fraction of Na is 0.0477. The normal freezing point of Hg is -39°C and its heat of fusion is 2331 J/mol.

7.51. Use the system in exercise 7.45 to calculate the osmotic pressure of the mercureous solution of sodium at 0°C. Assume a volume of 15.2 cm^3.

7.52. Use the system in exercise 7.45 to calculate the vapor pressure depression of mercury from the solution. The normal vapor pressure of Hg at 0°C is 0.000185 torr.

7.53. Calculate the cryoscopic and ebullioscopic constants for liquid bromine, Br_2. You will need the following data:

$\Delta_{fus}H$: 10.57 kJ/mol	MP: -7.2°C
$\Delta_{vap}H$: 29.56 kJ/mol	BP: 58.78°C

7.54. A 200,000-amu average molecular weight polymer is contaminated with 0.5% of a 100-amu impurity, presumably the monomer. Determine the error in the molecular weight determination if a 1.000×10^{-4} molal aqueous solution is used. Assume a temperature of 25.0°C.

7.55. Consider an aqueous solution of a polymer that has an average molecular weight of 185,000 amu. Calculate the molality that is needed to exert an osmotic pressure of 30 Pa at 37°C. How many grams per kilogram of solvent is this?

7.56. Derive equation 7.49.

Symbolic Math Exercises

7.57. The vapor pressures of benzene and 1,1-dichloroethane at 25.0°C are 94.0 and 224.9 mmHg, respectively. Plot the total pressure versus the mole fraction of benzene *in the solution.* Plot the total pressure versus the mole fraction of 1,1-dichloroethane.

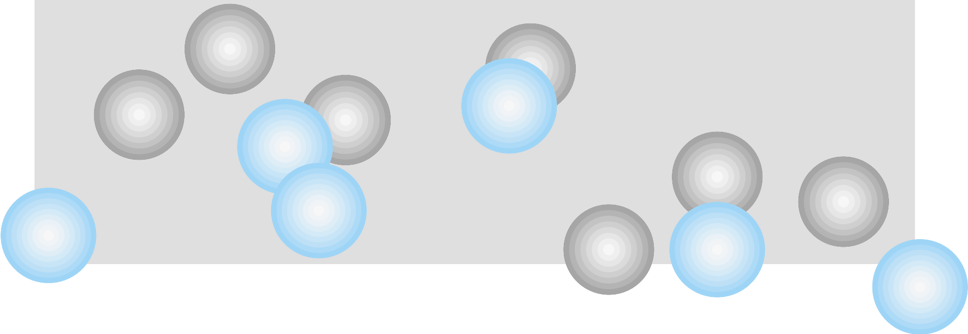
7.58. The vapor pressures of benzene and 1,1-dichloroethane at 25.0°C are 94.0 and 224.9 mmHg, respectively. What does a plot of total pressure versus the mole fraction of benzene *in the vapor* look like? What does a plot of total pressure versus the mole fraction of 1,1-dichloroethane look like? Compare these plots with your plots from exercise 7.57.

7.59. Consider your plots from 7.57 and 7.58 above. **(a)** Identify the dew point line(s). **(b)** Identify the bubble point line(s). **(c)** Using a combination of two appropriate lines, trace the fractional distillation of a 50:50 mole ratio of benzene and 1,1-dichloroethane, draw the theoretical plates, and predict the composition of the initially distilled product.

7.60. Tabulate the solubility of naphthalene in toluene between -50°C and 70°C in 5° increments. The heat of fusion of $C_{10}H_8$ is 19.123 kJ/mol and its melting point is 78.2°C.

8

Electrochemistry and Ionic Solutions



MUCH OF CHEMISTRY INVOLVES SPECIES that have charge. Electrons, cations, and anions are all charged particles that interact chemically. Often electrons move from one chemical species to another to form something new. These movements can be spontaneous, or they can be forced. They can involve systems as simple as hydrogen and oxygen atoms, or as complex as a million-peptide protein chain.

The presence and the value of discrete charges on chemical species introduces a new aspect that we must consider, the fact that like charges repel and opposite charges attract. In considering how charged particles interact, we have to understand the work involved in moving charged particles together and apart, and the energy required to perform that work. Energy, work—these are concepts of thermodynamics. Therefore, our understanding of the chemistry of electrically charged particles, *electrochemistry,* is based on thermodynamics.

Few people realize the widespread application of electrochemistry in modern life. All batteries and fuel cells can be understood in terms of electrochemistry. Any oxidation-reduction process can be considered in electrochemical terms. Corrosion of metals, nonmetals, and ceramics is electrochemistry. Many vitally important biochemical reactions involve the transfer of charge, which is electrochemistry. As the thermodynamics of charged particles are developed in this chapter, realize that these principles are widely applicable to many systems and reactions.

8.1 Synopsis

First, we will review the physics of charge interaction, which was understood fairly early in the development of modern science. It is easy to relate thermodynamic quantities, especially ΔG, to the work and energy involved in moving charged species. We can divide every electrochemical reaction into an oxidation part, in which some species loses electrons, and a reduction part, in which some species gains electrons. We will find that we can keep these parts separate and combine them to generate new electrochemical processes.

Electrochemical reactions are dependent on the quantity of charged species present, but because opposite charges attract each other, the simple specification of concentration does not necessarily correlate with behavior. The concepts of ionic strength, activity, and activity coefficients help us correlate the amount of charge with the behavior of the system.

It is also important to understand why ionic solutions behave the way they do. A few simple assumptions lead us to the Debye-Hückel theory for the description of ionic solutions. Even brief descriptions of these ideas will help us recognize why we devote an entire chapter to the interaction and chemistry of charged solutes.

8.2 Charges

Perhaps one of the earliest understandings of the scientific world is the concept of *charge.* In about the seventh century B.C., the Greek philosopher Thales found that a resinous substance called *elektron*—which we call amber—attracted light objects like feathers and thread after it had been rubbed. Through the centuries, people learned that amber rods or glass rods repel each other after being rubbed, but an amber rod and a glass rod attract each other. However, after touching, they immediately lose their attraction. In or around 1752, multitalented American Benjamin Franklin performed his (perhaps apocryphal) key and kite experiment with lightning, showing that it could induce the same properties in amber as rubbing it. It was Franklin who suggested that this phenomenon called electricity had opposing properties, which he labeled *positive* and *negative.* Franklin suggested that when one rubs a glass rod, electricity flows into it to make it positive. When one rubs an amber rod, electricity flows out of it, making it negative. When two oppositely charged rods touch, there is an exchange between the two until the amount of electricity is equalized. Two rods of the same charge, positive or negative, would avoid, or *repel,* each other. (Though amazingly prescient, Franklin was wrong about the charge that actually moved. However, vestiges of Franklin's definitions—especially with respect to the direction of current flow in an electrical circuit—are still common today.)

In the century that followed Franklin, other researchers like Coulomb, Galvani, Davy, Volta, Tesla, and Maxwell placed an understanding of electrical phenomena on solid experimental and theoretical grounds. This section reviews some of those grounds.

In 1785, the French scientist Charles de Coulomb (Figure 8.1) made very accurate measurements of the force of attraction or repulsion between small charged spheres. He found that the direction of the interaction—that is, attraction or repulsion—is dictated by the types of the charges on the spheres. If two spheres have the same charge, either positive or negative, they repel each other. If, however, the two spheres have different charges, they attract each other.

Coulomb also found that the magnitude of the interaction between any two spheres is dependent on the distance between the two small spheres. The force of attraction or repulsion, F, between two charged spheres varies inversely with the square of the distance, r, between the spheres:

$$F \propto \frac{1}{r^2} \tag{8.1}$$

It was found that the force between charged objects is also proportional to the magnitude of the charges, represented by q_1 and q_2, on the objects. Equation 8.1 becomes

$$F \propto \frac{q_1 \cdot q_2}{r^2} \tag{8.2}$$

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Figure 8.1 Charles-Augustin de Coulomb (1736–1806) was a French physicist who used very delicate (for the time) instrumentation to make measurements on the force of attraction between charged bodies.

This equation is known as *Coulomb's law.* In order to get the correct unit of force, newtons, from equation 8.2, an additional expression is included in the denominator of the equation. The complete SI form of Coulomb's law is

$$F = \frac{q_1 \cdot q_2}{4\pi\epsilon_0 \cdot r^2} \tag{8.3}$$

where q_1 and q_2 are in units of C and r is in units of m. The term 4π in the denominator is due to the three-dimensionality of space.* The term ϵ_0 ("epsilon naught") is called the *permittivity of free space.* Its value is $8.854 \times 10^{-12}\ \mathrm{C^2/(J{\cdot}m)}$, and its units allow for the proper algebraic conversion from units of charge and distance to units of force. Because the q's can be positive or negative, by convention F is positive for forces of repulsion and negative for forces of attraction.

Example 8.1

Calculate the force between charges in the following cases.

a. $+1.6 \times 10^{-18}$ C and $+3.3 \times 10^{-19}$ C at a distance of 1.00×10^{-9} m

b. $+4.83 \times 10^{-19}$ C and -3.22×10^{-19} C at a distance of 5.83 Å

Solution

a. Using equation 8.3, we substitute:

$$F = \frac{(+1.6 \times 10^{-18}\ \mathrm{C})(+3.3 \times 10^{-19}\ \mathrm{C})}{4\pi \cdot 8.854 \times 10^{-12}\dfrac{\mathrm{C^2}}{\mathrm{J{\cdot}m}} \cdot (1.00 \times 10^{-9}\ \mathrm{m})^2}$$

The coulomb units cancel, as does one of the meter units. The joule unit is in the denominator of the denominator, which ultimately places it in the numerator. Evaluating the numerical expression, we find that

$$F = +4.7 \times 10^{-9}\ \frac{\mathrm{J}}{\mathrm{m}} = +4.7 \times 10^{-9}\ \mathrm{N}$$

In the final step, we have used the fact that 1 J = 1 N·m. The positive value for the force indicates that it is a force of repulsion. This is a very small force for macroscopic objects, but a very large force for atom-sized systems, like ions.

b. A similar substitution yields

$$F = \frac{(+4.83 \times 10^{-19}\ \mathrm{C})(-3.22 \times 10^{-19}\ \mathrm{C})}{4\pi \cdot 8.854 \times 10^{-12}\dfrac{\mathrm{C^2}}{\mathrm{J{\cdot}m}} \cdot (5.83 \times 10^{-10}\ \mathrm{m})^2}$$

where the distance of 5.83 Å has been converted to standard units of meters. Solving:

$$F = -4.1 \times 10^{-9}\ \mathrm{N}$$

In this case, because the force is negative, it represents a force of attraction between the two charged bodies.

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*Actually, 4π is related to the three-dimensional coordinate system used to define space, and the fact that the force is spherically symmetric and depends only on the distance between particles. This factor will appear again in our discussion of spherical polar coordinates in Chapter 11.

Equations 8.2 and 8.3 involve the force due to electrical charges in a vacuum. If the electrical charges are in some medium other than vacuum, then a correction factor called the *dielectric constant,* ϵ_r, of that medium appears in the denominator of the equation for the force. Equation 8.3 becomes

$$F = \frac{q_1 \cdot q_2}{4\pi\epsilon_0 \cdot \epsilon_r \cdot r^2} \tag{8.4}$$

Dielectric constants are unitless. The higher the dielectric constant, the smaller the force between the charged particles. Water, for example, has a dielectric constant of about 78.

The *electric field E* of a charge q_1 interacting with another charge q_2 is defined as the force between the charges divided by the magnitude of the charge itself. Therefore, we have

$$E = \frac{F}{q_1} = \frac{q_2}{4\pi\epsilon_0 \cdot r^2} \tag{8.5}$$

in a vacuum. (Again, for a nonvacuum medium, we would add the dielectric constant of the medium in the denominator.) The magnitude of the electric field $|E|$ (the electric field is technically a vector) is the derivative with respect to position of some quantity called the *electric potential* ϕ:

$$|E| \equiv -\frac{\partial\phi}{\partial r}$$

Electric potential represents how much energy an electric particle can acquire as it moves through the electric field. We can rewrite this equation and integrate with respect to position r:

$$-|E| \cdot dr = d\phi$$

$$\int(-|E| \cdot dr) = \int d\phi$$

$$\phi = -\int |E| \cdot dr$$

Since we have an expression for E in terms of r (equation 8.5), we can substitute:

$$\phi = -\int \frac{q_2}{4\pi\epsilon_0 \cdot r^2}\, dr$$

This integral is solvable, since it is a function of r (that is, r to the second power in the denominator; all other variables are constant). We get

$$\phi = -\frac{q_2}{4\pi\epsilon_0}\int \frac{1}{r^2}\, dr$$

Evaluating:

$$\phi = \frac{q_2}{4\pi\epsilon_0 r} \tag{8.6}$$

The units for electric potential, based on this expression, are J/C. Since we will be working with electric potentials quite a bit, we define a new unit, volt (V), such that

$$1 \text{ V} = 1 \text{ J/C} \tag{8.7}$$

The unit volt is named in honor of the Italian physicist Alessandro Volta, who enunciated many fundamental ideas about electrochemical systems.

8.3 Energy and Work

How are these ideas related to energy, the principal quantity of thermodynamics? Let us consider work. We usually define work in terms of pressure-volume work. This is not the only kind of work that can be defined. For work involving charges, the definition is different. The infinitesimal amount of electrical work, dw_{elect}, is defined as the infinitesimal change in amount of charge, dQ, moving through some electric potential ϕ:

$$dw_{\text{elect}} \equiv \phi \cdot dQ \tag{8.8}$$

Since electric potential has units of V and charge has units of C, equation 8.7 shows that the unit for work using equation 8.8 is joules. Now that we are considering a new kind of work, we must remember to include this as part of the total change in internal energy under the first law of thermodynamics. That is, the infinitesimal change in the internal energy is now

$$dU = dw_{pV} + dq + dw_{\text{elect}}$$

This is not a *change* in the definition of internal energy. It is simply including another type of work. There are actually many contributions to work, and so far we have considered only pressure-volume work. Other types of non-pV work include not just electrical (that is, potential-charge), but also surface tension–area, gravitational-mass, centrifugal-mass, and others. However, we will consider only electrical work in this chapter.

Electrical work is performed by the movement of electrons, which are the charged particles that move around in the course of chemical reactions. (The proton has exactly the opposite charge, but in normal chemical reactions, it remains confined to the nucleus.) One of the properties of a single electron is that it has a specific charge, about 1.602×10^{-19} C. This value is symbolized by the letter e. (For an electron, the charge is symbolized as $-e$, and for the oppositely charged proton, the charge is $+e$.) In molar quantities, $e \cdot N_A$ (N_A = Avogadro's number) equals about 96,485 C/mol. This quantity is called *Faraday's constant* (in honor of Michael Faraday) and is symbolized by $\mathcal{F}$. Ions that have a positive charge of $+z$ therefore represent $z \cdot \mathcal{F}$ of positive charge per mole of ions, and ions having a negative charge of $-z$ represent $-z \cdot \mathcal{F}$ of negative charge per mole.

The infinitesimal change in charge dQ is related to the infinitesimal change in moles of ions, dn (where n is the number of moles of ions). Using the expressions from the previous paragraph, we can say that

$$dQ = z \cdot \mathcal{F} \cdot dn$$

Substituting this expression for dQ into equation 8.8, the infinitesimal amount of work is

$$dw_{\text{elect}} = \phi \cdot z \cdot \mathcal{F} \cdot dn \tag{8.9}$$

For multiple ions, the amount of work required to change the number of charged species labeled with an i subscript is

$$dw_{\text{elect}} = \sum_i \phi_i \cdot z_i \cdot \mathcal{F} \cdot dn_i \tag{8.10}$$

In a system where there is a transfer of charge, the number of species having any particular charge is changing, so in equation 8.10, dn_i is not zero. If we want to consider the infinitesimal change in G, we have to modify the natural variable equation for G, given by equation 4.48:

$$dG = -S\,dT + V\,dp + \sum_i \mu_i\,dn_i$$

to include the change in work due to the electric charges. We get

$$dG = -S\,dT + V\,dp + \sum_i \mu_i\,dn_i + \sum_i \phi_i \cdot z_i \cdot \mathcal{F} \cdot dn_i \tag{8.11}$$

Under conditions of constant temperature and pressure, this equation becomes

$$dG = \sum_i \mu_i\,dn_i + \sum_i \phi_i \cdot z_i \cdot \mathcal{F} \cdot dn_i$$

which can be rearranged algebraically because both of the sums are summing over the same index (the component i) and the same variable (the change in amount, dn_i):

$$dG = \sum_i (\mu_i + \phi_i \cdot z_i \cdot \mathcal{F}) \cdot dn_i \tag{8.12}$$

If we redefine the quantity inside the parentheses in equation 8.12 as $\mu_{i,\text{el}}$:

$$\mu_{i,\text{el}} \equiv \mu_i + \phi_i \cdot z_i \cdot \mathcal{F} \tag{8.13}$$

then we have

$$dG = \sum_i \mu_{i,\text{el}} \cdot dn_i \tag{8.14}$$

$\mu_{i,\text{el}}$ is called the *electrochemical potential,* rather than the chemical potential. For electrochemical equilibrium, the equation analogous to equation 5.4 ($\Sigma\mu_i\nu_i = 0$) is

$$\sum_i n_i \cdot \mu_{i,\text{el}} = 0 \tag{8.15}$$

This is the basic equation for electrochemical equilibrium.

Any reaction that involves a transfer of charge (that is, electrons) is an oxidation-reduction reaction, or *redox* reaction. Since an oxidation process and a reduction process always occur together, let us adopt a Hess's-law approach by considering each individual process independently, and then consider the overall process as the sum of the two individual reactions. Species A is being oxidized; the general chemical reaction can be represented as

$$A \longrightarrow A^{n+} + ne^-$$

where species A has lost n electrons, symbolized ne^-. Species B is being reduced. The general chemical reaction for this can be represented as

$$B^{n+} + ne^- \longrightarrow B$$

The overall chemical reaction is

$$A + B^{n+} \longrightarrow A^{n+} + B$$

Keeping in mind that the n_i values are positive for the reactants and negative for products, equation 8.15 becomes

$$0 = \mu_{A^{n+},\text{el}} + \mu_{B,\text{el}} - \mu_{A,\text{el}} - \mu_{B^{n+},\text{el}}$$

Using equation 8.13, and recognizing that we are requiring the same charge n on the ionic species, we have

$$0 = \mu_{A^{n+}} + \mu_B + n\mathcal{F}\phi_{\text{red}} - \mu_A - \mu_{B^{n+}} - n\mathcal{F}\phi_{\text{ox}} \tag{8.16}$$

where we are now labeling each ϕ as the potential from either the oxidation reaction ("ox") or the reduction reaction ("red"). Since the species A and B have no charge, there is no electrical work term (that is, equation 8.10) on their chemical potentials.

The oxidation and reduction electric potential terms do *not* cancel from equation 8.16. The electric potential of A^{n+} is not going to be the same as the electric potential from B^{n+}. (Consider the following comparison. Will the electric potential of an Li^+ ion be the same as that for a Cs^+ ion only because they have the same charge? Of course not. Li^+ has completely different properties from Cs^+.)

Rearranging equation 8.16:

$$n\mathcal{F}\phi_{ox} - n\mathcal{F}\phi_{red} = \mu_{A^{n+}} + \mu_B - \mu_A - \mu_{B^{n+}}$$

$$n\mathcal{F}(\phi_{ox} - \phi_{red}) = \mu_{A^{n+}} + \mu_B - \mu_A - \mu_{B^{n+}}$$

By convention, we rewrite the left side of the equation by substituting $-(\phi_{red} - \phi_{ox})$ for $(\phi_{ox} - \phi_{red})$:

$$-n\mathcal{F}(\phi_{red} - \phi_{ox}) = \mu_{A^{n+}} + \mu_B - \mu_A - \mu_{B^{n+}} \tag{8.17}$$

All of the terms on the right side of equation 8.17 are constant for a given state (pressure, temperature, and so on) of a system. Therefore, the entire right side of equation 8.17 is a constant. This means that the left side of equation 8.17 must be constant, also. The variables n and $\mathcal{F}$ are constants for the chemical reaction. Therefore, the expression $(\phi_{red} - \phi_{ox})$ must also be a constant for the reaction.

We define the *electromotive force, E*, as the difference between the reduction reaction's electric potential and the oxidation's electric potential:

$$E \equiv \phi_{red} - \phi_{ox} \tag{8.18}$$

Because ϕ values are expressed in units of volts, electromotive forces are expressed in units of volts. The letters EMF are sometimes used to stand for electromotive force. EMFs are not true "forces" in the scientific sense. Rather, they are changes in electric potential.

Equation 8.17 becomes

$$-n\mathcal{F}E = \mu_{A^{n+}} + \mu_B - \mu_A - \mu_{B^{n+}} \tag{8.19}$$

Now consider the right side of equation 8.19. It is the chemical potential of the products minus the chemical potential of the reactants. This equals the change in the Gibbs free energy of the reaction, $\Delta_{rxn}G$. Equation 8.19 can be rewritten as

$$\Delta_{rxn}G = -n\mathcal{F}E \tag{8.20}$$

Under standard conditions of pressure and concentration, this is

$$\Delta_{rxn}G^\circ = -n\mathcal{F}E^\circ \tag{8.21}$$

This is the basic equation for relating changes in electric potential with changes in energy. This equation also takes advantage of the definition that $1\ J = 1\ V{\cdot}C$. The variable n represents the number of moles of electrons that are transferred in the balanced redox reaction. Because completed redox reactions do not usually show the balanced number of electrons explicitly, we might have to figure this out from the redox reaction itself.

Example 8.2

a. What is the number of electrons transferred in the course of the following simple redox reaction?

$$2Fe^{3+}\ (aq) + 3Mg\ (s) \longrightarrow 2Fe\ (s) + 3Mg^{2+}\ (aq)$$

b. If the standard change in the Gibbs free energy of the molar reaction in part a is −1354 kJ, what is the difference between the reduction reaction's electric potential and the oxidation reaction's electric potential?

Solution

a. The easiest way to determine the number of electrons transferred is to separate the individual oxidation and reduction processes. This is easily done:

$$2\text{Fe}^{3+}\ (\text{aq}) + 6\text{e}^- \longrightarrow 2\text{Fe}\ (\text{s})$$

$$3\text{Mg}\ (\text{s}) \longrightarrow 3\text{Mg}^{2+}\ (\text{aq}) + 6\text{e}^-$$

The two reactions show that 6 electrons are transferred in the course of the balanced redox reaction. In molar units, there would be 6 moles of electrons transferred.

b. Using equation 8.21 after converting the units on $\Delta_{\text{rxn}}G°$ to joules:

$$-1{,}354{,}000\ \text{J} = -(6\ \text{mol e}^-)\left(96{,}485\ \frac{\text{C}}{\text{mol e}^-}\right)\cdot E°$$

$$E° = 2.339\ \text{V}$$

The unit of volts follows from equation 8.7.

There is one thing to notice about the signs on the electromotive force. Because ΔG is related to the spontaneity of an isothermal, isobaric process (that is, ΔG is positive for a nonspontaneous process, negative for a spontaneous process, and zero for equilibrium) and because of the negative sign in equation 8.21, we can establish another spontaneity test for an electrochemical process. If E is *positive* for a redox process, it is spontaneous. If E is *negative*, the process is not spontaneous. If E is zero, the system is at (electrochemical) equilibrium. Table 8.1 summarizes the spontaneity conditions.

Table 8.1 A summary of spontaneity conditions

If ΔG is	If E is	Then the process is
Negative	Positive	Spontaneous
Zero	Zero	At equilibrium
Positive	Negative	Not spontaneous

Just because a redox reaction occurs doesn't mean that anything electrochemically useful is happening. In order to get something useful from a redox reaction (besides the chemical outcome), a redox reaction must be set up properly. But even if a redox reaction is set up properly, how much can we expect to get out of the differences in the electric potentials?

The answer lies in the fact that E, the difference in electric potentials, is related to the change in the Gibbs free energy of the reaction, equation 8.21. Furthermore, we showed in Chapter 4 that if some non-pressure-volume type of work is performed on or by the system, ΔG for that change represents a limit to the amount of non-pV work that can be performed:

$$\Delta G \leq w_{\text{non-}pV}$$

This was equation 4.11. Since electrical work is a type of non-pV work, we can state that

$$\Delta G \leq w_{\text{elect}} \tag{8.22}$$

Since work done *by* the system has a negative numerical value, we can restate equation 8.22 by saying that ΔG for a redox reaction represents the maximum amount of electrical work that the system can do on the surroundings.


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Figure 8.2 (a) Zinc metal is added to a blue solution containing Cu^{2+} ions. (b) The zinc has reacted to make colorless Zn^{2+} ions and the blue Cu^{2+} ions have reduced to Cu metal. Although a redox reaction has occurred, no useful work has been obtained from this physical system.

How do we extract this work? Figure 8.2a shows a solution containing Cu^{2+} ions and some zinc metal. In Figure 8.2b, zinc has been added to the solution. The colored Cu^{2+} ions have reacted to make solid Cu metal, while

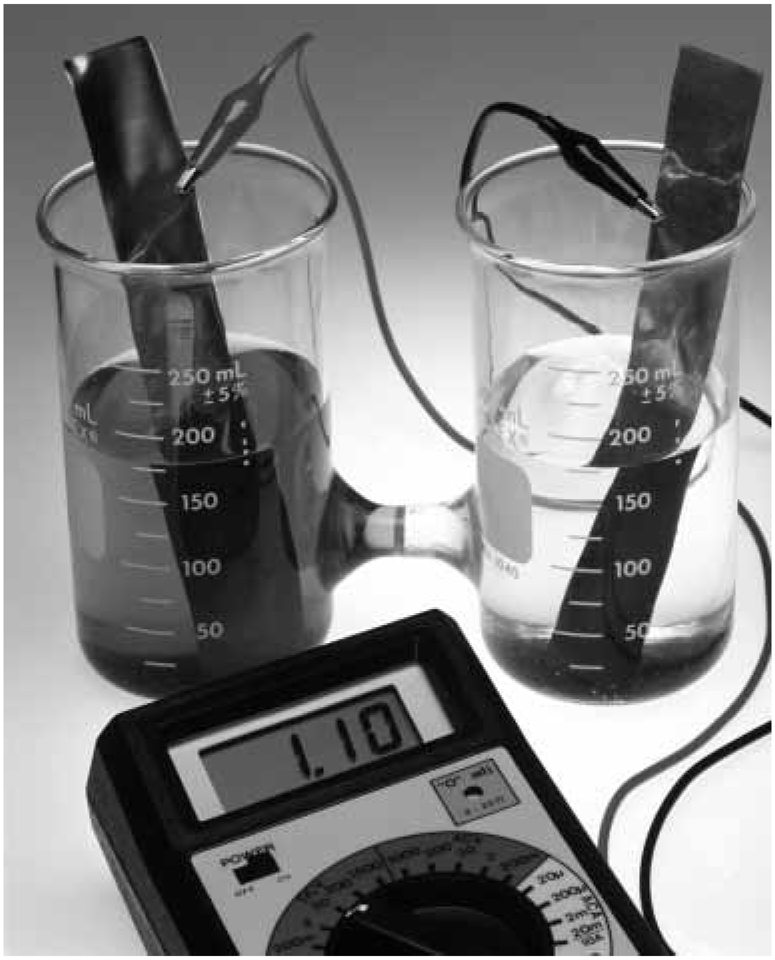

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Figure 8.3 The same redox reaction as in Figure 8.2 is shown, but now each half-reaction is physically separate from the other. As this redox reaction occurs, we can extract useful work from the transfer of electrons, as shown.

the zinc metal has reacted to colorless Zn^{2+} ions. The spontaneous redox reaction is

$$Zn\ (s) + Cu^{2+} \longrightarrow Zn^{2+} + Cu\ (s) \qquad E° = +1.104\ V$$

However, in this example, the reaction occurred spontaneously and we were not able to extract any useful work out of the reaction.

Suppose we were to set up the same reaction, but with the oxidation and reduction *half-reactions* physically separated, as in Figure 8.3. On the left side, zinc metal can be oxidized to zinc ions, and on the right side the copper ions are reduced to copper metal. The two half-reactions aren't completely separated. A *salt bridge* connects them to maintain an overall charge balance. The salt bridge allows positive ions to flow into the reduction side of the system, and negative ions to flow into the oxidation side of the system. In both cases, this acts to preserve the electrical neutrality of each side.* Some conducting medium, usually a wire, connects the two metal *electrodes*. If we attach some electrical device such as a voltmeter or a lightbulb to the wire, we can operate the device: we can extract work from the spontaneous electrochemical reaction, as shown in Figure 8.3. By separating the individual half-reactions, we can get energy in terms of electrical work from the spontaneous chemical reaction.

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*Other methods besides salt bridges are also used to maintain charge balance.

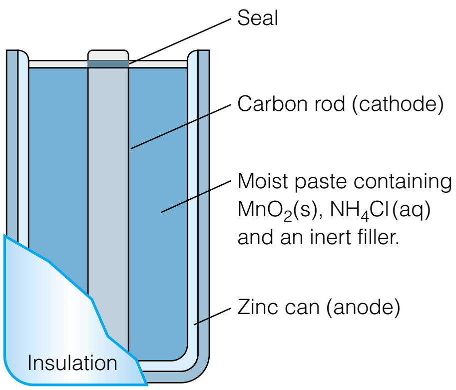

Figure 8.4 A modern battery is more complicated than a simple Daniell cell, but the electrochemical principles are the same.

The two independent, physical systems that contain the reactions are called *half-cells*. The half-cell that contains the oxidation reaction is called the *anode*, and the half-cell containing the reduction reaction is called the *cathode*. The two half-cells together make up a system that, for a spontaneous reaction, is called a *voltaic cell* or *galvanic cell*. All batteries are voltaic cells, although their redox chemistry and construction may not be as simple as the battery illustrated in Figure 8.3. (The zinc/copper voltaic cell is called a *Daniell cell* after the English chemist John Daniell, who developed it in 1836. At the time, it was the most reliable source of electricity.) Figure 8.4 shows a detailed diagram of a modern voltaic cell.

Systems in which nonspontaneous reactions are forced to proceed by the intentional introduction of electrons are called *electrolytic cells*. Such cells are used for electroplating metals onto jewelry and metalware, among other uses.

Keep in mind that the calculated value of ΔG for an electrochemical process represents the maximum amount of electric work that the reaction can do. In reality, less than that maximum is actually extracted. This is a consequence of the less than 100% efficiency of all processes.

8.4 Standard Potentials

Recall that E, the electromotive force, is originally defined as the difference between the reduction potential and the oxidation potential. Do we know the *absolute* electromotive force for any individual reduction or oxidation process? Unfortunately, we don't. The situation is very much like internal energy, or any other kind of energy. We understand that there is some absolute amount of energy in a system, we accept the fact that we can never know exactly how much energy there is in a system, but we do know that we can follow *changes* in the energy of a system. It is the same thing with E.

In order to keep track of the energies of a system, we defined certain standards, like the heats of formation of compounds, with the recognition that the heats of formation of elements in their standard states are exactly zero. We do something similar for electromotive forces. The conventions we use for defining *standard potentials* are as follows:

- We consider the separate half-reactions rather than balanced redox reactions. This way, any redox reaction can be constructed by algebraically combining the appropriate two (or more) half-reactions.
- Typically, we speak of the potential for a half-reaction as that half-reaction written as a *reduction* reaction. When combining two (or more) reactions, at least one must be reversed to express it as an oxidation reaction. When reversing a reaction, the standard potential changes sign.
- For standard potentials, the standard thermodynamic conditions of pressure and concentration are presumed, and are usually given at the common reference temperature of 25°C. That is, if we are using a standard potential for a half-reaction, it is assumed that the reaction is occurring at 25°C, a fugacity of 1 for gaseous species, and an activity of 1 for dissolved species. (A common approximation is 1 atm or 1 bar for gases and 1 M for dissolved species.)
- The standard potential for the reduction half-reaction

$$2H^+\ (aq) + 2e^- \longrightarrow H_2\ (g) \qquad \textbf{(8.23)}$$

is defined as 0.000 V. This is the reaction of the *standard hydrogen electrode*, or SHE (Figure 8.5). All other standard potentials are defined with respect to this half-reaction.

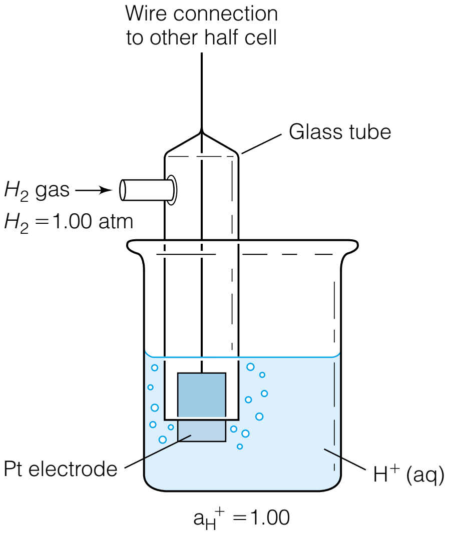

Figure 8.5 The standard hydrogen electrode. The half-reaction occurring in this electrode has been assigned a standard reduction potential of exactly 0.000 V.

Table 8.2 Standard reduction potentials

Reaction	$E°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.866
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.776
$N_2O + 2H^+ + 2e^- \rightarrow N_2 + H_2O$	1.766
$Au^+ + e^- \rightarrow Au$	1.692
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.679
$HClO_2 + H^+ + 3e^- \rightarrow \frac{1}{2}Cl_2 + 2H_2O$	1.63
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	1.5415
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.507
$Au^{3+} + 3e^- \rightarrow Au$	1.498
$Cl_2 + 2e^- \rightarrow 2\ Cl^-$	1.358
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229
$Br_2 + 2e^- \rightarrow 2Br^-$	1.087
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{\ 2+}$	0.920
$Hg^{2+} + 2e^- \rightarrow Hg$	0.851
$Ag^+ + e^- \rightarrow Ag$	0.7996
$Hg_2^{\ 2+} + 2e^- \rightarrow 2Hg$	0.7973
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.771
$MnO_4^- + e^- \rightarrow MnO_4^{\ 2-}$	0.558
$I_3^- + 2e^- \rightarrow 3I^-$	0.536
$I_2 + 2e^- \rightarrow 2I^-$	0.5355
$Cu^+ + e^- \rightarrow Cu$	0.521
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.401
$Cu^{2+} + 2e^- \rightarrow Cu$	0.3419
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.26828
$AgCl + e^- \rightarrow Ag + Cl^-$	0.22233
$Cu^{2+} + e^- \rightarrow Cu^+$	0.153
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.151
$AgBr + e^- \rightarrow Ag + Br^-$	0.07133
$2H^+ + 2e^- \rightarrow H_2$	0.0000
$Fe^{3+} + 3e^- \rightarrow Fe$	−0.037
$2D^+ + 2e^- \rightarrow D_2$	−0.044
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.1262
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.1375
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.257
$Co^{2+} + 2e^- \rightarrow Co$	−0.28
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{\ 2-}$	−0.3588
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.407
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.447
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.744
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.7618
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.8277
$Cr^{2+} + 2e^- \rightarrow Cr$	−0.913
$Al^{3+} + 3e^- \rightarrow Al$	−1.662
$Be^{2+} + 2e^- \rightarrow Be$	−1.847
$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.372
$Na^+ + e^- \rightarrow Na$	−2.71
$Ca^{2+} + 2e^- \rightarrow Ca$	−2.868
$Li^+ + e^- \rightarrow Li$	−3.04

These points define the standard electrochemical reduction potentials, represented by $E°$. A list of standard reduction potentials is given in Table 8.2. You should know and be able to apply these conventions in order to successfully work with electrochemistry.

As an aside, it should be pointed out that conventions do change occasionally. It used to be the convention to list half-reactions as *oxidation* reactions, not reduction reactions. You may occasionally find an old book or table that lists half-reactions in that manner, and you should be cautious. Also, the SHE is not the only possible standard electrode against which other half-reactions can be measured. Another common one is the *saturated calomel electrode,* which is based on the half-reaction

$$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg\ (\ell) + 2Cl^- \tag{8.24}$$

$$E° = +0.2682 \text{ V versus SHE}$$

(The common name for mercury(I) chloride is calomel.) This half-reaction is sometimes preferable because it doesn't use hydrogen gas, which is a potential explosion hazard. If it is used, then all of the standard reduction potentials are shifted by 0.2682 V from the standard reduction potentials listed with respect to SHE.

In order to use the standard potentials for an electrochemical reaction of interest, simply separate the reaction into its half-reactions, find the standard potential from a table, reverse one (or more) of the reactions to make it an oxidation reaction, and negate (that is, change the sign of) its $E°$ value. A properly balanced redox reaction has no leftover electrons, so one or more of the reactions must be multiplied by some integral constant so that the electrons cancel. However, the $E°$ values *are not multiplied by that same constant.* E's are electric potentials and are *intensive* variables, which are defined as independent of the amount (as opposed to *extensive* variables, which are dependent on the amount).

Finally, standard potentials are strictly additive only for overall electrochemical reactions in which there are no unbalanced electrons. If there are unbalanced electrons in the overall reactions, the $E°$ values are not strictly additive. Consider as an example the following:

$$Fe^{3+} + 3e^- \xrightarrow{\text{rxn 1}} Fe\ (s) \qquad E° = -0.037 \text{ V}$$

$$Fe\ (s) \xrightarrow{\text{rxn 2}} Fe^{2+} + 2e^- \qquad E° = +0.447 \text{ V}$$

$$\text{Overall rxn:} \quad Fe^{3+} + e^- \xrightarrow{\text{overall rxn}} Fe^{2+} \qquad E° \overset{?}{=} +0.410 \text{ V}$$

A look at Table 8.2 shows that the reduction reaction $Fe^{3+} + e^- \rightarrow Fe^{2+}$ has an $E°$ of 0.771 V, nowhere close to the predicted 0.410 V. $E°$ values are not additive if electrons do not cancel.

However, by Hess's law, *energies* are additive. What must be done for the above example is to convert each $E°$ into an equivalent $\Delta G°$, add the $\Delta G°$ values together for the overall reaction as allowed by Hess's law, and then convert the final $\Delta G°$ into a final $E°$ for the new half-reaction. For the above example, we get

$$\text{Rxn 1:} \quad \Delta G° = -(3 \text{ mol e}^-)\left(96{,}485\ \frac{\text{C}}{\text{mol e}^-}\right)(-0.037 \text{ V}) = 10{,}700 \text{ J}$$

$$\text{Rxn 2:} \quad \Delta G° = -(2 \text{ mol e}^-)\left(96{,}485\ \frac{\text{C}}{\text{mol e}^-}\right)(+0.409 \text{ V}) = -86{,}300 \text{ J}$$

Applying Hess's law, the overall ΔG value for the process is

$$\Delta G^\circ_{\text{overall}} = \Delta G^\circ\ (\text{Rxn } 1) + \Delta G^\circ\ (\text{Rxn } 2) = 10{,}400 - 75{,}600\ \text{J}$$

$$\Delta G^\circ_{\text{overall}} = -68{,}500\ \text{J}$$

Converting this into an equivalent E gives

$$-68{,}500\ \text{J} = -(1\ \text{mol e}^-)\left(96{,}485\ \frac{\text{C}}{\text{mol e}^-}\right) \cdot E^\circ_{\text{overall}}$$

$$E^\circ_{\text{overall}} = +0.783\ \text{V}$$

which is much closer to the number from the standard reduction potential table. (The difference is related to the differing activities of the iron ions in the solutions.) The key point is that electric potentials are strictly additive only if the electrons cancel completely. However, energies are *always* additive.

Example 8.3

a. What is E° for the following unbalanced reaction?

$$\text{Fe (s)} + \text{O}_2\ \text{(g)} + 2\text{H}_2\text{O}\ (\ell) \longrightarrow \text{Fe}^{3+} + 4\text{OH}^-$$

(The ultimate products are FeO(OH) and H_2O, but they are formed by a nonredox reaction. The hydrated FeO(OH) is what we know as rust.)

b. Balance the reaction.

c. What are the conditions of the above process?

Solution

a. With the help of Table 8.2, we find that the above reaction can be separated into the two half-reactions

$$\text{Fe (s)} \longrightarrow \text{Fe}^{3+} + 3\text{e}^- \qquad E^\circ = +0.037\ \text{V}$$

$$\text{O}_2\ \text{(g)} + 2\text{H}_2\text{O}\ (\ell) + 4\text{e}^- \longrightarrow 4\text{OH}^- \qquad E^\circ = +0.401\ \text{V}$$

We do not have to balance the reaction yet, since we can determine the overall E° value by combining the two E° values above. We get

$$E^\circ = +0.438\ \text{V}$$

The reaction is spontaneous, and actually represents a summary reaction for the corrosion of iron.

b. Electrons must cancel in a balanced electrochemical (that is, redox) reaction. Since the oxidation reaction involves three electrons and the reduction reaction involves four, the lowest common multiple is 12 and we get

$$4\text{Fe (s)} + 3\text{O}_2\ \text{(g)} + 6\text{H}_2\text{O}\ (\ell) \longrightarrow 4\text{Fe}^{3+}\ \text{(aq)} + 12\text{OH}^-\ \text{(aq)}$$

as the balanced chemical reaction.

c. Because of the ° superscript on the E, we must assume that the following conditions apply to the reaction: 25°C, a fugacity of 1 for O_2 and an activity of 1 for Fe (s), H_2O (ℓ), Fe^{3+} (aq), and OH^- (aq). [Again, these conditions are usually approximated by 1 bar (or atm) pressure for the gaseous reactants, and 1 M concentration for the aqueous, dissolved ions.]

As you might suspect, in real life the corrosion of iron does not occur at standard conditions, especially standard conditions of concentration. We need additional tools to determine the electromotive force at nonstandard conditions.

Many complex biochemical reactions are electron-transfer processes, and as such have a standard reduction potential. For example, nicotinamide adenine dinucleotide (NAD^+) accepts a proton and two electrons to become NADH:

$$NAD^+ + H^+ + 2e^- \longrightarrow NADH \qquad E° = -0.105 \text{ V}$$

under standard conditions. The potentials for one-electron reductions of iron in myoglobin ($E' = +0.046$ V) and cytochrome *c* ($E' = 0.254$ V) listed here are for *biochemical* standard states (that is, pH = 7; 37°C). Thus, when considering biochemical processes, it is crucial to understand what the conditions are for the reactions of interest.

8.5 Nonstandard Potentials and Equilibrium Constants

Example 8.3 assumed that the conditions of the reaction were standard thermodynamic conditions. However, in reality this is almost never the case. Reactions occur in highly variable conditions of temperature, concentration, and pressure. (Indeed, many electrochemically based reactions occur at tiny concentrations of ions. Consider the rusting of your car.)

Standard and nonstandard *E*'s for electrochemical reactions follow the same rules as energies: if it is a standard *E*, then the symbol *E* has the ° on it. However, if the *E* is simply some instantaneous electromotive force for any immediate set of conditions, then the ° sign is left off: *E*.

The most well-known relationship between *E* and *E*° is the *Nernst equation*, derived by the German chemist Walther Hermann Nernst (Figure 8.6) in 1889. (Among other achievements, Nernst was the principal enunciator of the third law of thermodynamics, was the first to explain explosions in terms of branching chain reactions, and invented the Nernst glower, a useful source of infrared radiation. He received the 1920 Nobel Prize in Chemistry for his contributions in thermodynamics.) Having recognized the validity of the following two equations:

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Figure 8.6 Walther Hermann von Nernst (1864–1941), a German chemist who first formulated an equation relating the potential of an electrochemical reaction to the instantaneous conditions of the products and reactants. His Nobel Prize, however, was awarded in honor of his pioneering work to establish the third law of thermodynamics.

$$\Delta G = -n\mathcal{F}E$$

$$\Delta G = \Delta G° + RT \ln Q$$

(these are equations 8.20 and 5.7, respectively), one can combine them to yield

$$-n\mathcal{F}E = -n\mathcal{F}E° + RT \ln Q$$

Solving for *E*, the nonstandard electromotive force:

$$E = E° - \frac{RT}{n\mathcal{F}} \ln Q \tag{8.25}$$

which is the Nernst equation. Recall that *Q* is the reaction quotient, which is expressed in terms of the instantaneous (nonequilibrium) concentrations, pressures, activities, or fugacities of reactants and products.

Example 8.4

Given the nonstandard concentrations for the following reaction, calculate the instantaneous *E* of the Daniell cell.

$$Zn + Cu^{2+} \text{ (0.0333 M)} \longrightarrow Zn^{2+} \text{ (0.00444 M)} + Cu$$

Solution

The expression for Q is

$$Q = \frac{\dfrac{m_{\mathrm{Zn}^{2+}}}{m^\circ}}{\dfrac{m_{\mathrm{Cu}^{2+}}}{m^\circ}} \approx \frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]}$$

which is 0.00444/0.0333 = 0.133. Given that the voltage under standard conditions, E°, is 1.104 V, we have

$$E = 1.104\ \mathrm{V} - \frac{(8.314\ \frac{\mathrm{J}}{\mathrm{mol\cdot K}})(298\ \mathrm{K})}{(2\ \mathrm{mol\ e^-})(96{,}485\ \frac{\mathrm{C}}{\mathrm{mol\ e^-}})} \ln(0.133)$$

All of the units cancel except for the expression J/C, which equals the unit volt. Solving:

$$E = 1.104\ \mathrm{V} - (-0.0259\ \mathrm{V})$$

$$E = 1.130\ \mathrm{V}$$

This is slightly greater than the standard voltage.

The Nernst equation is very useful for estimating the voltage of electrochemical cells at nonstandard conditions of concentration or pressure. But despite the fact that the Nernst equation contains temperature, T, as a variable, it has limited use at temperatures other than 25°C, the common reference temperature. That's because E° itself varies with temperature. We can estimate how E° varies with temperature by considering the following two expressions:

$$\Delta G^\circ = -n\mathcal{F}E^\circ$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \text{or} \quad \left[\frac{\partial(\Delta G)}{\partial T}\right]_p = -\Delta S$$

Combining them, we find that

$$\left[\frac{\partial(\Delta G^\circ)}{\partial T}\right]_p = -n\mathcal{F}\left(\frac{\partial E^\circ}{\partial T}\right)_p = -\Delta S^\circ$$

where we have now included the ° symbol on G, E, and S. Solving for the change in E° with respect to the change in temperature (that is, $\partial E^\circ/\partial T$), we get

$$\left(\frac{\partial E^\circ}{\partial T}\right)_p = \frac{\Delta S^\circ}{n\mathcal{F}} \qquad \textbf{(8.26)}$$

The derivative $(\partial E^\circ/\partial T)_p$ is called the *temperature coefficient* of the reaction. Equation 8.26 can be rearranged and approximated as

$$\Delta E^\circ \approx \frac{\Delta S^\circ}{n\mathcal{F}}\Delta T \qquad \textbf{(8.27)}$$

where ΔT is the change in temperature from the reference temperature (usually 25°C). Keep in mind that this is the change in the EMF of a process, so the new EMF at the nonreference temperature is

$$E \approx E^\circ + \Delta E^\circ \qquad \textbf{(8.28)}$$

These equations are approximations, but fairly good ones. We aren't even considering the change in ΔS° as the temperature changes—those can be substantial, as we saw in previous chapters. But equations 8.26 and 8.27 do provide a rough guide about the behavior of an electrochemical system as temperature changes. Since $\mathcal{F}$ is a relatively large number, the change in $E°$ is slight as the temperature changes, but there can be a noticeable effect for some common electrochemical reactions.

Example 8.5

Estimate E for the following reaction at 500 K:

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (g)$$

This is the chemical reaction for fuel cells, which among other uses provide electrical power to the space shuttle.

Solution

First, we determine $E°$ under standard conditions. The above reaction can be broken down into the half-reactions

$$2 \times (H_2\ (g) \longrightarrow 2H^+ + 2e^-) \qquad E° = 0.000\ \text{V}$$

$$O_2\ (g) + 4H^+ + 4e^- \longrightarrow 2H_2O\ (\ell) \qquad E° = 1.229\ \text{V}$$

The standard EMF for the reaction is therefore 1.229 V.

$\Delta S°$ for the reaction is determined by looking up $S°$ values for H_2, O_2, and H_2O (all in the gaseous state) in Appendix 2. We get

$$\Delta_{\text{rxn}}S° = 2(188.83) - [2(130.68) + (205.14)]\ \tfrac{\text{J}}{\text{K}}$$

$$\Delta_{\text{rxn}}S° = -88.84\ \tfrac{\text{J}}{\text{K}}$$

for the molar reaction. The change in temperature is 500 K − 298 K = 202 K. Using equation 8.27, we can estimate the change to $E°$:

$$\Delta E° \approx \frac{\Delta S°}{n\mathcal{F}}\Delta T = \frac{-88.84\ \tfrac{\text{J}}{\text{K}}}{(4\ \text{mol e}^-)(96{,}485\ \tfrac{\text{C}}{\text{mol e}^-})}(202\ \text{K})$$

$$\Delta E° \approx -0.0465\ \text{V}$$

so that the approximate voltage of the reaction at 500 K is

$$E \approx 1.229 - 0.0465$$

$$E \approx 1.183\ \text{V}$$

This is a slight but noticeable decrease.

We can easily rearrange equation 8.26 to get an expression for $\Delta S°$:

$$\Delta S° = n\mathcal{F}\frac{\partial E°}{\partial T} \tag{8.29}$$

Now that we have expressions for $\Delta G°$ and $\Delta S°$, we can find an expression for $\Delta H°$. Using the original definition for ΔG (that is, $\Delta G = \Delta H - T\Delta S$), we get

$$-n\mathcal{F}E° = \Delta H° - T\left(n\mathcal{F}\frac{\partial E°}{\partial T}\right)$$

We rearrange this algebraically to get

$$\Delta H° = -n\mathcal{F}\left(E° + T\frac{\partial E°}{\partial T}\right) \tag{8.30}$$

This equation allows us to calculate $\Delta H°$ for a process using electrochemical information.

Example 8.6

Consider the following formation reaction for H_2O (ℓ):

$$2H_2\text{ (g)} + O_2\text{ (g)} \longrightarrow 2H_2O\text{ }(\ell)$$

If $\Delta H° = 571.66$ kJ at 25°C and $n = 4$ for this reaction, determine the temperature coefficient of the standard potential $E°$.

Solution

We can use equation 8.30 to determine $\partial E°/\partial T$, which is the temperature coefficient of interest. Using Table 8.2, we can determine that $E°$ for the reaction is 1.23 V. Substituting into the equation for the known quantities:

$$571{,}660\text{ J} = (4\text{ mol e}^-)(96{,}500\text{ C/mol e}^-)\left[1.23\text{ V} + (298\text{ K})\frac{\partial E°}{\partial T}\right]$$

The "mol e^-" units cancel, and when we divide by Faraday's constant we get J/C as a unit, which equals a volt. We get

$$1.481\text{ V} = \left[1.23\text{ V} + (298\text{ K})\frac{\partial E°}{\partial T}\right]$$

$$0.25\text{ V} = (298\text{ K})\frac{\partial E°}{\partial T}$$

$$\frac{\partial E°}{\partial T} = 8.4 \times 10^{-4}\text{ V/K}$$

The final units are appropriate for a temperature coefficient of electromotive force.

Changes in E versus pressure aren't normally considered, since the expression

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

implies that

$$\left(\frac{\partial(\Delta G°)}{\partial p}\right)_T = -n\mathcal{F}\left(\frac{\partial E°}{\partial p}\right)_T = -\Delta V$$

and rearranging:

$$\left(\frac{\partial E°}{\partial p}\right)_T \approx \frac{\Delta V}{n\mathcal{F}} \tag{8.31}$$

Since most voltaic cells are based in some condensed phase (that is, liquid or solid), the change in volume of this condensed phase is very small unless pressure changes are very, very high. Since ΔV values are typically very small and $\mathcal{F}$ is numerically very large, we can ignore the pressure effects on $E°$. However, *partial* pressure variations of gaseous products or reactants involved in the electrochemical reaction can have a large effect on $E°$. These effects are usually handled with the Nernst equation, since the partial pressure of a reactant or product contributes to the value of the reaction quotient Q.

Finally, the relationship between the equilibrium constant and the EMF of a reaction should be considered. This relationship is commonly used to make measurements on various systems, by measuring the voltage across some contrived electrochemical cell. Using the relationships

$$\Delta G° = -n\mathcal{F}E°$$

$$\Delta G° = -RT\ln K$$

we can easily combine these two equations and derive the expression

$$E^\circ = \frac{RT}{n\mathcal{F}} \ln K \tag{8.32}$$

This expression can also be derived from the Nernst equation by considering the following: at equilibrium, $E = 0$ (that is, there is no potential difference between the cathode and the anode). But also at equilibrium, the expression Q is exactly the equilibrium constant K for the reaction. Therefore, the Nernst equation becomes

$$0 = E^\circ - \frac{RT}{n\mathcal{F}} \ln K$$

which rearranges to

$$E^\circ = \frac{RT}{n\mathcal{F}} \ln K$$

which is equation 8.32. Voltages of reactions at standard conditions can therefore be used to determine the equilibrium position of that reaction (at which point E equals 0).

Example 8.7

Using electrochemical data, what is the solubility product constant, K_{sp}, of AgBr at 25°C?

Solution

The chemical reaction representing the solubility of AgBr is

$$\text{AgBr (s)} \rightleftharpoons \text{Ag}^+ \text{ (aq)} + \text{Br}^- \text{ (aq)}$$

This can be written as the combination of two reactions from Table 8.2:

$$\text{AgBr (s)} + \text{e}^- \longrightarrow \text{Ag (s)} + \text{Br}^- \text{ (aq)} \qquad E^\circ = 0.07133 \text{ V}$$

$$\text{Ag (s)} \longrightarrow \text{Ag}^+ \text{ (aq)} + \text{e}^- \qquad E^\circ = -0.7996 \text{ V}$$

Therefore, for the overall reaction E° is -0.728 V. Using equation 8.32 (and assuming molar quantities):

$$-0.728 \text{ V} = \frac{(8.314 \, \frac{\text{J}}{\text{K}})(298 \text{ K})}{(1 \text{ mol e}^-)(96{,}485 \, \frac{\text{C}}{\text{mol e}^-})} \ln K_{sp}$$

Convince yourself that $n = 1$ in this example. All of the units on the right side except J/C cancel, and we should recognize this fraction to be equal to a volt unit, which cancels with the volt unit on the left side of the equation. Rearranging to isolate the natural logarithm of K_{sp}:

$$\ln K_{sp} = \frac{(-0.728)(1)(96{,}485)}{(8.314)(298)} = -28.4$$

Taking the inverse logarithm of both sides, we get our final answer:

$$K_{sp} = 4.63 \times 10^{-13}$$

At 25°C, K_{sp} for AgBr is measured as 5.35×10^{-13}, giving you an idea how closely it can be calculated using the electrochemical values.

The relationship between E and the reaction quotient Q has a practical use in modern analytical chemistry. Consider the standard reduction reaction for hydrogen:

$$2H^+ \text{ (aq)} + 2e^- \longrightarrow H_2 \text{ (g)}$$

Its defined $E°$ is zero, but at nonstandard conditions of concentration, E for this half-reaction will be determined by the Nernst equation. We will have, since $E°$ is zero:

$$E = -\frac{RT}{2\mathcal{F}} \ln Q = -\frac{RT}{2\mathcal{F}} \ln \frac{f_{H_2}}{(a_{H^+})^2} \approx -\frac{RT}{2\mathcal{F}} \ln \frac{p_{H_2}}{[H^+]^2}$$

Assume we are working at standard pressure so that $p_{H_2} = 1$ bar. Further, using the definition of $\text{pH} = -\log[H^+] = -\frac{1}{2.303} \ln [H^+]$ and the properties of logarithms, we can rearrange the equation for E using these expressions and get

$$E = -2.303 \cdot \frac{RT}{\mathcal{F}} \cdot \text{pH} \qquad \textbf{(8.33)}$$

At the common reference temperature of 25.0°C, the expression 2.303 $(RT/\mathcal{F})$ equals 0.05916 V. Equation 8.33 can be rewritten as

$$E = -0.05916 \cdot \text{pH volts} \qquad \textbf{(8.34)}$$

Thus, the reduction potential of the hydrogen electrode is directly related to the pH of the solution. What this means is that we can use the hydrogen electrode, coupled with any other half-reaction, to determine the pH of a solution. The voltage of the electrochemical cell that is made by the proper combination of such half-cells is given by the combination of the two E values of the reactions. Therefore,

$$E = (-0.05916 \text{ V} \cdot \text{pH}) + E° \text{ (other half-reaction)} \qquad \textbf{(8.35)}$$

where each term on the right has units of V. The value of "$E°$ (other half-reaction)" depends, of course, on what that reaction is as well as whether it is an oxidation reaction or a reduction reaction. The point is that the voltage of such cells can easily be measured and the pH of the solution determined using electrochemical means.

Because hydrogen electrodes are cumbersome, other electrodes are typically used to measure pH. All of them use similar electrochemical principles and a measurement of a voltage to determine the pH of a solution of interest. The most well known is the *glass pH electrode,* Figure 8.7. A porous glass tube has a certain buffer solution and a silver/silver chloride electrode. The Ag/AgCl half-reaction is

$$\text{AgCl (s)} + e^- \longrightarrow \text{Ag (s)} + \text{Cl}^- \qquad E° = 0.22233 \text{ V}$$

The buffer solution in the electrode is set so that $E = 0$ when the pH is about 7, and the electronics that monitor the voltage of the electrode can be adjusted to calibrate the system so that $E = 0$ at pH 7.00 exactly. Such electrodes are common in laboratories around the world.

The hydrogen ion is not special when it comes to electrochemical measurement of this type. Virtually every ionic species can take part in oxidation-reduction reactions, so the concentration of virtually any ion can be detected with a similar electrode. These *ion-specific electrodes* have some half-reaction inside and, across a porous glass shell, set up an electrochemical cell whose voltage can be measured and used to "back-calculate" the concentration of a

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Figure 8.7 Electrochemistry is the basis of pH measurement by instrumental means. Shown here is a glass pH electrode, whose *E* value is sensitive to the concentration of the H^+ ion.

particular ion. Figure 8.8 shows an ion-specific electrode. For the most part, they resemble pH electrodes, so care should be exercised to identify the exact ion an electrode detects.

Example 8.8

What is the pH of the solution phase of a hydrogen electrode that is connected to an Fe/Fe^{2+} half-reaction if the voltage of the spontaneous reaction is 0.300 V? Assume that the concentration of Fe^{2+} is 1.00 M and all other conditions are standard.

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Figure 8.8 H^+ is not the only ion whose concentration can be measured electrochemically. Shown here is a different ion-specific electrode. All of them use the instantaneous *E* of some electrochemical process to determine the concentration of the specific ion.

Solution

According to the half-reactions in Table 8.2, the only possible spontaneous reaction is the oxidation of Fe to Fe^{2+} and the reduction of H^+ to H_2 gas:

$$\mathrm{Fe\ (s) + 2H^+\ (aq, ??\ M) \longrightarrow Fe^{2+}\ (aq) + H_2\ (g)}$$

Because we are reversing the Fe standard reduction reaction, the value for "$E°$ (other half-reaction)" that we use in equation 8.35 is the negative of -0.447 V, or $+0.447$ V. Using equation 8.35, we have

$$0.300\ \mathrm{V} = (-0.05916\ \mathrm{V} \cdot \mathrm{pH}) + 0.447\ \mathrm{V}$$

Solving for pH:

$$-0.147 = -0.05916 \cdot \mathrm{pH}$$

$$\mathrm{pH} = 2.48$$

This is a fairly acidic pH, corresponding to an approximate concentration of 3.3 mM.

8.6 Ions in Solution

It is oversimplified to think that ions in solution behave "ideally" even for dilute solutions. For molecular solutes like ethanol or CO_2, interactions between solute and solvent are minimal or are dominated by hydrogen bonding or some other polar interaction. However, we usually assume that individual solute molecules do not strongly affect *each other*.

For ions in dilute solution, the presence of oppositely charged ions will affect the expected properties of the solution. *Dilute* ionic solutions have concentrations of 0.001 M or even less. (That's one-thousandth of a molarity unit. For comparison, seawater can be considered as about 0.5 M.) At such low concentrations, the molarity is almost numerically equal to the molality, which is the preferred unit for colligative properties (because then the solution properties do not depend on the identity of the solute). Therefore, we can shift from molarity concentration units to molality concentration units, and submit that dilute ionic solutions will have concentrations of 0.001 *m* or less.

In addition, the charge on the ion will also be a factor. Coulomb's law, equation 8.2, says that the force between charges is directly related to the product of the magnitudes of the charges. Therefore, the force of interaction between charges of $+2$ and -2 will be four times as great as between charges of $+1$ and -1. Thus, the behavior of dilute NaCl should be different from the behavior of dilute $ZnSO_4$, even if they are the same molal concentration.

As with other nonideal chemical systems, in order to better understand ionic solutions we will go back to the concepts of chemical potentials and activities. In Chapter 4, we defined the chemical potential μ_i of a material as the change in the Gibbs free energy versus the molar amount of that material:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p} \qquad \textbf{(8.36)}$$

We also defined the activity a_i of a component in a multicomponent system as some nonideal parameter that defines the actual chemical potential μ_i in terms of the standard chemical potential μ_i°:

$$\mu_i = \mu_i^\circ + RT \ln a_i \qquad \textbf{(8.37)}$$

In the case of gas mixtures, we defined activity as related to the partial pressure p_i of the gas. For ions in solution, the activity of the ionic solute is related to the concentration of the solute, in this case the molality:

$$a_i \propto m_i \tag{8.38}$$

We do the same thing mathematically with equation 8.38 as we have done with previous proportionalities. In order to remove the unit of molality, we divide the right side of equation 8.38 by some standard concentration $m°$, which we set at exactly 1 molal. We also use the proportionality constant γ_i, called the *activity coefficient,* for an ion:

$$a_i = \gamma_i \cdot \frac{m_i}{m°} \tag{8.39}$$

The value of the activity coefficient γ_i varies with concentration, so we must either tabulate the values versus concentration or have a way of calculating them. However, in the limit of infinite dilution, ionic solutions should behave as if their molal concentration is directly related to the chemical potential; that is,

$$\lim_{m_i \to 0} \gamma_i = 1 \tag{8.40}$$

As concentrations of ions get larger, γ_i gets smaller, and the activity gets progressively smaller and smaller than the true molal concentration of the ions.

The subscript i on the variables in the above equations implies that each individual species has its own molality, activity, activity coefficient, and so on. For example, in a 1.00-molal solution of sodium sulfate (Na_2SO_4),

$$m_{\mathrm{Na}^+} = 2.00 \text{ m}$$

$$m_{\mathrm{SO_4}^{2-}} = 1.00 \text{ m}$$

(Notice how we are subscripting the molal symbol with the appropriate ion.)

The fact that the total positive charge must equal the total negative charge implies a relationship between the charges on the ions and their molal concentrations. For a simple binary salt $A_{n_+}B_{n_-}$, where n_+ and n_- are the formula subscripts for the cation and anion, respectively, ionic solutions require that the molalities of the cation and anion satisfy the formula

$$\frac{\mathrm{m}_+}{n_+} = \frac{m_-}{n_-} \tag{8.41}$$

It is easy to verify this expression using our sodium sulfate solution. From the formula Na_2SO_4, we find by inspection that $n_+ = 2$ and $n_- = 1$:

$$\frac{2.00\ m}{2} = \frac{1.00\ m}{1}$$

Substituting for the activities of the cation a_+ and the anion a_- in equation 8.37, the chemical potentials of the cation and anion are

$$\mu_+ = \mu_+^\circ + RT \ln \gamma_+ \frac{m_+}{m°}$$

$$\mu_- = \mu_-^\circ + RT \ln \gamma_- \frac{m_-}{m°}$$

Because the $\mu°$ values and molalities of the positive and negative ions are not necessarily the same, the chemical potentials of the cation and anions will probably be different. The total chemical potential of the ionic solution depends, of course, on the number of moles of each ion, which are given by the ionic formula variables n_+ and n_-. The total chemical potential is

$$\mu = (n_+ \cdot \mu_+) + (n_- \cdot \mu_-) \tag{8.42}$$

Substituting for μ_+ and μ_- from above:

$$\mu = (n_+ \cdot \mu_+^\circ) + (n_- \cdot \mu_-^\circ) + \left(n_+ \cdot RT \ln \gamma_+ \frac{m_+}{m^\circ}\right) + \left(n_- \cdot RT \ln \gamma_- \frac{m_-}{m^\circ}\right)$$

This equation is simplified by defining the *mean ionic molality* $m_\pm$ and the *mean ionic activity coefficient* $\gamma_\pm$ as

$$m_\pm \equiv (m_+^{n_+} \cdot m_-^{n_-})^{1/(n_+ + n_-)} \tag{8.43}$$

$$\gamma_\pm \equiv (\gamma_+^{n_+} \cdot \gamma_-^{n_-})^{1/(n_+ + n_-)} \tag{8.44}$$

Further, if we define $n_\pm = n_+ + n_-$ and $\mu_\pm^\circ = n_+\mu_+^\circ + n_-\mu_-^\circ$, we can rewrite the expression for total chemical potential as

$$\mu = \mu_\pm^\circ + n_\pm RT \ln \gamma_\pm \frac{m_\pm}{m^\circ} \tag{8.45}$$

By analogy to equation 8.37, using the properties of logarithms we can define the mean ionic activity $a_\pm$ of an ionic solute $A_{n_+}B_{n_-}$ as

$$a_\pm = \left(\gamma_\pm \frac{m_\pm}{m^\circ}\right)^{n_\pm} \tag{8.46}$$

These equations indicate how ionic solutions will really behave.

Example 8.9

Determine the mean ionic molality and activity for a 0.200-molal solution of $Cr(NO_3)_3$ if its mean activity coefficient $\gamma_\pm$ is 0.285.

Solution

For chromium(III) nitrate, the coefficients n_+ and n_- are 1 and 3, respectively, so that $n_\pm$ is 4. The ideal molality of Cr^{3+} (aq) is 0.200 *m*, and the ideal molality of NO_3^- (aq) is 0.600 *m*. The mean ionic molality is therefore

$$m_\pm = (0.200^1 \cdot 0.600^3)^{1/4}\ m$$

$$m_\pm = 0.456\ m$$

Using this and the given mean activity coefficient, we can determine the mean activity of the solution:

$$a_\pm = \left(0.285 \cdot \frac{0.456\ m}{1.00\ m}\right)^4$$

$$a_\pm = 2.85 \times 10^{-4}$$

The behavior of this solution is based on a mean activity of 2.85×10^{-4}, rather than a molality of 0.200. This makes a big difference in the expected behavior of the solution.

Solutions containing ions that have larger absolute charges have greater coulombic effects affecting their properties. One way to keep track of this is by defining the *ionic strength, I*, of the solution:

$$I = \frac{1}{2} \sum_{i=1}^{\substack{\text{number of} \\ \text{ions}}} m_i \cdot z_i^2 \tag{8.47}$$

where z_i is the charge on the *i*th ion. Ionic strength was originally defined in 1921 by Gilbert N. Lewis. Recall that for ionic solutes that do not have a 1 : 1 ratio of cation and anion, the individual molalities m_i will not be the same. The following example illustrates.

Example 8.10

a. Calculate the ionic strengths of 0.100 *m* NaCl, Na_2SO_4, and $Ca_3(PO_4)_2$.
b. What molality of Na_2SO_4 is needed to have the same ionic strength as 0.100 *m* $Ca_3(PO_4)_2$?

Solution

a. Using equation 8.47, we can find that

$$I_{\mathrm{NaCl}} = \tfrac{1}{2}[(0.100\ m)(+1)^2 + (0.100\ m)(-1)^2] = 0.100\ m$$

$$I_{\mathrm{Na_2SO_4}} = \tfrac{1}{2}[(\underset{\underset{n_+=2}{\uparrow}}{2} \cdot 0.100\ m)(+1)^2 + (0.100\ m)(-2)^2] = 0.300\ m$$

$$I_{\mathrm{Ca_3(PO_4)_2}} = \tfrac{1}{2}[(\underset{\underset{n_+=3}{\uparrow}}{3} \cdot 0.100\ m)(+2)^2 + (\underset{\underset{n_-=2}{\uparrow}}{2} \cdot 0.100\ m)(-3)^2] = 1.50\ m$$

Notice how high the ionic strength gets when the charges on the individual ions increase.

b. This part asks what molality of Na_2SO_4 is needed to get an ionic strength the same as 0.100 *m* $Ca_3(PO_4)_2$, which we found in part a to be 1.50 *m*. We can set up the $I_{\mathrm{Na_2SO_4}}$ ionic strength expression, but use 1.50 *m* for the value and set the molality as the unknown. We have

$$I_{\mathrm{Na_2SO_4}} = 1.50\ m = \tfrac{1}{2}[(2 \cdot m)(+1)^2 + (m)(-2)^2]$$

$$1.50\ m = \tfrac{1}{2}(2m + 4m) = \tfrac{1}{2} \cdot 6\ m = 3\ m$$

Therefore,

$$m = 0.500\ m$$

So we need a solution of Na_2SO_4 with five times the molality to have the same ionic strength as $Ca_3(PO_4)_2$. As an exercise, what molality of NaCl would be needed to have this same ionic strength?

As with any other chemical species, solvated ions also have enthalpies and free energies of formation, and entropies. From equation 8.23, we can see that

$$\tfrac{1}{2}\mathrm{H_2}\ (\mathrm{g}) \longrightarrow \mathrm{H^+}\ (\mathrm{aq}) + 1\mathrm{e^-} \qquad E° = 0.000\ \mathrm{V}$$

This is (almost) the formation reaction of H^+ (aq) from its elements, and using the relationship between *E* and ΔG, we might suggest that $\Delta_f G[\mathrm{H^+(aq)}] = 0$. However, this argument presents a problem. First of all, the presence of the electron as a product is problematic in terms of defining this equation as the formation reaction of H^+. Second, in reality the formation of cations like H^+ is always accompanied by the formation of anions.

Just as we have defined the $\Delta_f H$ values of elements to be zero and used them as benchmarks to determine the heats of formations of compounds, we make a similar definition for ions. We *define* the standard enthalpy of formation and the standard free energy of formation of the hydrogen ion as zero:

$$\Delta_f G^\circ[H^+(aq)] = \Delta_f H^\circ[H^+(aq)] \equiv 0 \tag{8.48}$$

Thus, the enthalpies and free energies of formation of other ions can be measured relative to the aqueous hydrogen ion.

The same issue exists for entropies of ions: again, the entropy of any one ion cannot be experimentally separated from the entropy of an oppositely charged ion that must be present. Again, we get around this problem by defining the entropy of the hydrogen ion as zero:

$$S[H^+(aq)] \equiv 0 \tag{8.49}$$

Entropies of other ions are determined with respect to this benchmark.

The concept of free energies, enthalpies, and entropies of ions are complicated by the fact that these ions are forming in some solvent (most commonly, water). The values of $\Delta_f H$, $\Delta_f G$, and S have contributions from the solvent molecules rearranging due to the presence of the ion. Enthalpies and free energies of formation, and even entropies, may be higher or lower than those for H^+ (aq) (that is, they may be positive or negative) depending in part on the solvation effects. Trends in thermodynamic values for ions may be difficult to explain unless these effects are taken into account. Note, too, that this implies that entropies of ions may be negative, in apparent contradiction with the very concept of absolute entropy and the third law of thermodynamics. You must keep in mind that the entropies of ions are determined with respect to those of H^+ and, as such, ions may have higher or lower entropies.

Example 8.11

a. Determine $\Delta_f H^\circ[Cl^-(aq)]$ if the enthalpy of reaction for

$$\tfrac{1}{2}H_2\ (g) + \tfrac{1}{2}Cl_2\ (g) \longrightarrow H^+\ (aq) + Cl^-\ (aq)$$

is −167.2 kJ.

b. Determine $\Delta_f H^\circ[Na^+\ (aq)]$ if the enthalpy of reaction for

$$NaCl\ (s) \longrightarrow Na^+\ (aq) + Cl^-\ (aq)$$

is +3.9 kJ. Use $\Delta_f H^\circ[NaCl] = -411.2$ kJ. Assume standard conditions for all species in both reactions.

Solution

a. If standard conditions are assumed, we know that $\Delta_f H^\circ[H_2(g)] = \Delta_f H^\circ[Cl_2(g)] = 0$. By definition, $\Delta_f H^\circ[H^+(aq)] = 0$, so if we know that $\Delta_{rxn} H$ is −167.2 kJ, we have

$$-167.2\text{ kJ} = \sum \Delta_f H[\text{prods}] - \sum \Delta_f H[\text{reacts}]$$

$$-167.2\text{ kJ} = (\Delta_f H[Cl^-(aq)] + 0) - (0 + 0)$$

$$-167.2\text{ kJ} = \Delta_f H[Cl^-(aq)]$$

b. Using the enthalpy of formation of Cl^- (aq) from part a, we can apply the same tactic to the dissolution of sodium chloride:

$$+3.9\text{ kJ} = \sum \Delta_f H[\text{prods}] - \sum \Delta_f H[\text{reacts}]$$

$$+3.9\text{ kJ} = [\Delta_f H[\text{Na}^+(\text{aq})] + (-167.2)] - (-411.2)$$

$$-240.1\text{ kJ} = \Delta_f H[\text{Na}^+(\text{aq})]$$

Entropies and free energies of formation for ions are determined similarly.

8.7 Debye-Hückel Theory of Ionic Solutions

Ionic strength is a useful concept because it allows us to consider some general expressions that depend only on ionic strength and not on the identities of the ions themselves. In 1923, Peter Debye and Erich Hückel made some simplifying assumptions about all ionic solutions. They assumed that they would be dealing with very dilute solutions, and that the solvent was basically a continuous, structureless medium that has some dielectric constant ϵ_r. Debye and Hückel also assumed that any deviations in solution properties from ideality were due to the coulombic interactions (repulsions and attractions) between the ions.

Applying some of the tools of statistics and the concept of ionic strength, Debye and Hückel derived a relatively simple relationship between the activity coefficient $\gamma_\pm$ and the ionic strength I of a dilute solution:

$$\ln \gamma_\pm = A \cdot z_+ \cdot z_- \cdot I^{1/2} \qquad \textbf{(8.50)}$$

where z_+ and z_- are the charges on the positive and negative ions, respectively. Note that the charge on the positive ion is itself positive, and the charge on the negative ion is itself negative. The constant A is given by the expression

$$A = (2\pi N_A \rho_{\text{solv}})^{1/2} \cdot \left(\frac{e^2}{4\pi\epsilon_0\epsilon_r kT}\right)^{3/2} \qquad \textbf{(8.51)}$$

where:

N_A = Avogadro's number

ρ_{solv} = density of solvent (in units of kg/m^3)

e = fundamental unit of charge, in C

ϵ_0 = permittivity of free space

ϵ_r = dielectric constant of solvent

k = Boltzmann's constant

T = absolute temperature

Equation 8.50 is the central part of what is called the *Debye-Hückel theory* of ionic solutions. Since it strictly applies only to very dilute solutions ($I < 0.01$ m), this expression is more specifically known as the *Debye-Hückel limiting law*. Because A is always positive, the product of the charges $z_+ \cdot z_-$ is always negative, so $\ln \gamma_\pm$ is always negative. This implies that $\gamma_\pm$ is always less than 1, which in turn implies that the solution is not ideal.

There is one important thing to observe about the Debye-Hückel limiting law. It depends on the identity of the solvent, since the density and dielectric constant of the solvent are part of the expression for A. But the limiting law has no variable dictated by the ionic solute except for the charges on the ions! It is seemingly independent of the identity of the *solute*. This implies that, for example, dilute NaCl and dilute KBr solutions have the same properties, since they are composed of ions having the same charges. However, dilute NaCl and dilute $CaSO_4$ would have different properties, despite both being 1 : 1 ionic salts, since the charges on the respective cations and anions are different.

For more precise calculations, the size of the ions involved is a factor also. Rather than calculating an average activity coefficient $\gamma_\pm$, individual ionic activity coefficients γ_+ and γ_- are considered here. A more precise expression from Debye-Hückel theory for the activity coefficient of an individual ion is

$$\ln \gamma = -\frac{A \cdot z^2 \cdot I^{1/2}}{1 + B \cdot å \cdot I^{1/2}} \tag{8.52}$$

where z is the charge on the ion, å represents the ionic diameter (in units of meters), and B is another constant given by the expression

$$B = \left(\frac{e^2 N_A \rho_{\text{solv}}}{\epsilon_0 \epsilon_r kT}\right)^{1/2} \tag{8.53}$$

All of the variables were defined above. I still represents the ionic strength of the solution, which contains contributions from *both* ions. Because z^2 is positive whether z is positive or negative, the negative sign in equation 8.52 ensures that $\ln \gamma$ is always negative, so that γ is always less than 1. Equation 8.52 is sometimes called the *extended Debye-Hückel law*.

Equation 8.52 is like equation 8.50 in that the activity coefficient (and therefore the activity) is dependent only on properties of the solvent and the charge and size of the ion, but not the chemical identity of the ion itself. It is therefore not uncommon to see tables of data in terms of å and the ionic charge rather than the individual ions themselves. Table 8.3 is such a table. In using data from tables like this, you must be extremely careful to make sure the units work out properly. All units should cancel, leaving a unitless number for the

Table 8.3 Activity coefficients by charge, ionic size, and ionic strength

	Ionic strength I^a				
å (10^{-10} m)	0.001	0.005	0.01	0.05	0.10
±1-charged ions					
9	0.967	0.933	0.914	0.86	0.83
7	0.965	0.930	0.909	0.845	0.81
5	0.964	0.928	0.904	0.83	0.79
3	0.964	0.925	0.899	0.805	0.755
±2-charged ions					
8	0.872	0.755	0.69	0.52	0.45
6	0.870	0.749	0.675	0.485	0.405
4	0.867	0.740	0.660	0.445	0.355
±3-charged ions					
6	0.731	0.52	0.415	0.195	0.13
5	0.728	0.51	0.405	0.18	0.115
4	0.725	0.505	0.395	0.16	0.095

Source: J. A. Dean, ed., *Lange's Handbook of Chemistry,* 14th ed., McGraw-Hill, New York, 1992.

[a] Values in this section are for the activity coefficient, γ.

logarithm of γ. However, you may have to apply appropriate conversions in order for the units to cancel properly.

How well do these equations work? First, we will consider equation 8.50, the simplified Debye-Hückel limiting expression. The experimental values for $\gamma_\pm$ for 0.001-molal HCl and $CaCl_2$ at 25°C are 0.966 and 0.888, respectively. The ionic strengths of the two solutions are 0.001 *m* and 0.003 *m*. In aqueous solution, the value for *A* is

$$A = (2\pi N_A \rho_{\text{solv}})^{1/2}\left(\frac{e^2}{4\pi\epsilon_0\epsilon_r kT}\right)^{3/2}$$

$$= \left(2\pi \cdot 6.02 \times 10^{23}\,\text{mol}^{-1} \cdot 997\frac{\text{kg}}{\text{m}^3}\right)^{1/2} \times \left(\frac{(1.602 \times 10^{-19}\ \text{C})^2}{4\pi \cdot 8.854 \times 10^{-12}\,\frac{\text{C}^2}{\text{J}\cdot\text{m}} \cdot 78.54 \cdot 1.381 \times 10^{-23}\,\frac{\text{J}}{\text{K}} \cdot 298\ \text{K}}\right)^{3/2}$$

where we have used the density of water as 997 kg/m^3 at 25°C and a dielectric constant of 78.54, and the rest of the variables are fundamental constants that can be obtained from tables.

Ultimately, the units work out to $\text{kg}^{1/2}/\text{mol}^{1/2}$, which is the reciprocal of the square root of the molality unit, $(\text{molal})^{-1/2}$. Numerically, the overall value of *A* comes out as

$$A = 1.171\ \text{molal}^{-1/2} \tag{8.54}$$

(This value of *A* is good for any aqueous solution at 25°C.) For HCl, in which $z_+ = +1$ and $z_- = -1$, we have

$$\ln \gamma_\pm = (1.171\ \text{molal}^{-1/2}) \cdot +1 \cdot -1 \cdot \sqrt{0.001\ \text{molal}}$$

Notice how the square root of the molal units cancel. Numerically we have

$$\ln \gamma_\pm = -0.03703$$

Therefore,

$$\gamma_\pm = 0.964$$

This value is very close to the experimental value of 0.966. For $CaCl_2$, we have

$$\ln \gamma_\pm = (1.171\ \text{molal}^{-1/2}) \cdot +2 \cdot -1 \cdot \sqrt{0.003\ \text{molal}} = -0.1283$$

$$\gamma_\pm = 0.880$$

which is again very close to the experimental value of 0.888. Even the simple form of the Debye-Hückel limiting law works very well for dilute solutions. The more precise expression for the Debye-Hückel law is really necessary only for more concentrated solutions.

Using Debye-Hückel theory, we can determine the activity coefficients of ionic solutions. From these activity coefficients, we can determine the activities of ions in a solution. The activities of ions, in turn, are related to the molalities—that is, the concentrations—of ions in a solution. We must therefore modify our approach in our understanding of the behavior of ionic solutions. (Indeed, this idea applies to all solutions, but we are considering only ionic solutions here.) Rather than relating the concentration of a solution to its measurable properties, it is more accurate to relate the measurable properties of an ionic solution *to the activities of the ions*. Thus, equations like equation 8.25 are better expressed as

$$E = E^\circ - \frac{RT}{n\mathcal{F}} \ln Q$$

$$= E^\circ - \frac{RT}{n\mathcal{F}} \ln \frac{\Pi_i a_i(\text{prods})^{\nu_i}}{\Pi_j a_j(\text{reacts})^{\nu_j}} \tag{8.55}$$

where we have redefined Q, the reaction quotient, as

$$Q = \frac{\Pi_i a_i(\text{prods})^{\nu_i}}{\Pi_j a_j(\text{reacts})^{\nu_j}} \tag{8.56}$$

where a_i(prods) and a_j(reacts) are the *activities* of the product and reactant species, respectively. The exponents ν_i and ν_j are the stoichiometric coefficients of the products and reactants, respectively, from the balanced chemical equation. The values for γ in Table 8.3 suggest that as ionic solutions become more concentrated, properties like E for an electrochemical reaction are less accurately predicted using concentrations but more accurately predicted using activities. The following example illustrates the difference.

Example 8.12

a. Approximate the expected voltage for the following electrochemical reaction using the given molal concentrations.

$$2\text{Fe (s)} + 3\text{Cu}^{2+} \text{ (aq, 0.050 molal)} \longrightarrow 2\text{Fe}^{3+} \text{ (aq, 0.100 molal)} + 3\text{Cu (s)}$$

b. Again approximate the expected voltage, but this time use the calculated activities according to the Debye-Hückel theory.

The reaction occurs at 25.0°C. The value for B at this temperature is $2.32 \times 10^9 \text{ m}^{-1} \cdot \text{molal}^{-1/2}$. A is still 1.171 $\text{molal}^{-1/2}$.

Assume that the molal concentrations are close enough to molar concentrations that they can be used directly. Additionally, assume that the anion is NO_3^-, that is, that we are in reality considering 0.050-molal $Cu(NO_3)_2$ and 0.100-molal $Fe(NO_3)_3$ solutions. Also, use the fact that the average ionic radii for Fe^{3+} and Cu^{2+} are 9.0 Å and 6.0 Å, respectively.

Solution

Using Table 8.2, we can easily determine that $E^\circ = 0.379$ V and that the number of electrons transferred in the course of the molar reaction is 6.

a. Using the molal concentrations in the Nernst equation:

$$E = 0.379 \text{ V} - \frac{(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(298 \text{ K})}{(6 \text{ mol e}^-)(96{,}485 \frac{\text{C}}{\text{mol e}^-})} \ln \frac{(0.1)^2}{(0.05)^3}$$

$$E = (0.379 - 0.00188) \text{ V} = 0.377 \text{ V}$$

b. If, however, we use the Debye-Hückel formula, we first have to calculate the activity coefficients of the ions:

$$\ln \gamma_{Fe^{3+}} = -\frac{1.171 \text{ molal}^{-1/2} \cdot (+3)^2 \cdot (0.600 \text{ molal})^{1/2}}{1 + 2.32 \times 10^9 \text{ m}^{-1} \cdot \text{molal}^{-1/2} \cdot 9.00 \times 10^{-10} \text{ m} \cdot (0.600 \text{ molal})^{1/2}}$$

where we have converted the ionic radius of Fe^{3+} to units of meters and have used the calculated ionic strength of a 0.100-molal $Fe(NO_3)_3$ solution. We get

$$\ln \gamma_{Fe^{3+}} = -3.119$$

$$\gamma_{Fe^{3+}} = 0.0442$$

This means that the activity of Fe^{3+} is

$$a_{Fe^{3+}} = 0.0442\,\frac{0.100\text{ molal}}{1.00\text{ molal}} = 0.00442$$

Similarly, we can calculate that the activity coefficient for Cu^{2+} is

$$\gamma_{Cu^{2+}} = 0.308$$

Therefore, the activity for Cu^{2+} is

$$a_{Cu^{2+}} = 0.308\,\frac{0.0500\text{ molal}}{1.00\text{ molal}} = 0.0154$$

Using activities instead of concentrations, we find that

$$E = 0.379\text{ V} - \frac{(8.314\,\frac{\text{J}}{\text{mol}\cdot\text{K}})(298\text{ K})}{(6\text{ mol e}^-)(96{,}485\,\frac{\text{C}}{\text{mol e}^-})}\ln\frac{(0.00442)^2}{(0.0154)^3}$$

$$E = (0.379 - 0.00718)\text{ V} = 0.372\text{ V}$$

Surely, the difference in the two calculated E values is not a large difference in voltages. But it is an easily measurable one, and for precise measurements the difference can have a big impact on the predicted properties of the ionic solution. For example, it is necessary to consider activity factors when using pH and other ion-selective electrodes, because the exact voltage of the electrochemical cell that is made in the course of the measurement is dependent on the activity of the ions involved, not their concentration. Activity, like fugacity, is a more realistic measure of how real chemical species behave. For precise calculations, activity must be used for ionic solutions, not concentration.

8.8 Ionic Transport and Conductance

One additional property that solutions of ionic solutes have and solutions of non-ionic solutions don't is that ionic solutions conduct electricity. The word *electrolyte* is used to describe ionic solutes, for that reason. (The word *nonelectrolyte* is used to describe those solutes whose solutions do not conduct electricity.) This property of electrolytes had deep ramifications in the basic understanding of ionic solutions, as demonstrated by Svante Arrhenius in 1884. Arrhenius (Figure 8.9) actually proposed in his doctoral thesis that electrolytes are compounds composed of oppositely charged ions that separate when they dissolve, thereby allowing them to conduct electricity. He passed with the lowest possible grade. However, with the increasing evidence of the electrical nature of atoms and matter, he was awarded the third Nobel Prize in Chemistry, in 1903, for his work.

AIP Emilio Segre Visual Archives

Figure 8.9 Svante Arrhenius (1859–1927), a Swedish chemist who laid the groundwork for the understanding of ionic solutions. Although he barely passed his doctoral examination, this same work won him a Nobel Prize in Chemistry.

The conductivity of ionic solutions is due to movement of both cations and anions. They move in opposite directions (as might be expected), and so we can consider a current due to positive ions, I_+, and a current due to negative ions, I_-. If we consider the current as the change in the amount of ions passing through a cross-sectional area A per unit time, as shown in Figure 8.10, then we can write the current as

$$I_+ = \frac{\partial q_+}{\partial t}$$

$$I_- = \frac{\partial q_-}{\partial t}$$

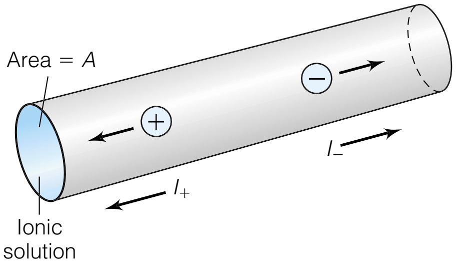

Figure 8.10 Ionic current travels in two directions, and is measured in terms of how many ions pass through some cross-sectional area *A* per unit time.

In molar amounts, if we recognize that the total charge (positive or negative) equals the magnitude of the charge times the fundamental unit of charge (e) times the number of moles of ions, we can rewrite the above equations as

$$I_i = e \cdot |z_i| \cdot \frac{\partial N_i}{\partial t} \tag{8.57}$$

where N_i represents the number of ions of species i. The absolute value on the charge of the ion ensures that the current will be positive.

Assuming that the ions are moving with some velocity v_i through the cross-sectional area A, and expressing the concentration of the ion as N/V (that is, amount divided by volume), we can write the change in amount per unit time, $\partial N_i/\partial t$, as the concentration times the area times the velocity, or

$$\frac{\partial N_i}{\partial t} = \frac{N_i}{V} A \cdot v_i$$

Substituting into equation 8.57:

$$I_i = e \cdot |z_i| \cdot \frac{N_i}{V} \cdot A \cdot v_i$$

Ions conducting current in solution are moving in response to an electromotive force acting across the solution. Recall from equation 8.5 that there is a relationship between force F and the electric field E:

$$F_i = q_i \cdot E$$

which we can rewrite using e and the charge on the ion:

$$F_i = e \cdot |z_i| \cdot E$$

Newton's second law says that if a force is acting on an object, the object accelerates and increases its velocity. If there is some ever-present force due to the electric field, then an ion should accelerate forever (or until it physically hits an electrode). However, in solution, there is also a force of friction due to movement through the solvent (just like a swimmer feels a "drag" from the water in a pool). This force of friction always works against the direction of motion, and is proportional to the velocity of the ion. Therefore, we can write

$$\text{force of friction on ion} = f \cdot v_i$$

where f is the proportionality constant. The force on the ion, F_i, becomes

$$F_i = e \cdot |z_i| \cdot E - f \cdot v_i \tag{8.58}$$

Because of the force of friction, at some velocity the net force on the ion will drop to zero and the ion will no longer accelerate. Its velocity will remain constant. According to equation 8.58, this terminal velocity can be derived as follows:

$$0 = e \cdot |z_i| \cdot E - f \cdot v_i$$

$$v_i = \frac{e \cdot |z_i| \cdot E}{f} \tag{8.59}$$

But what is f, the frictional proportionality constant? According to *Stokes' law*, the frictional constant of a spherical body with radius r_i moving through a fluid medium with a viscosity η is

$$f = 6\pi\eta r_i \tag{8.60}$$

Viscosity is typically measured in units of poise, where

$$1 \text{ poise} \equiv 1 \frac{\text{g}}{\text{cm}\cdot\text{s}}$$

Using the expression for Stokes' law, the velocity of the ions becomes

$$v_i = \frac{e \cdot |z_i| \cdot E}{6\pi\eta r_i}$$

Substituting into the expression for current, I_i becomes

$$I_i = e^2 \cdot |z_i|^2 \cdot \frac{N_i}{V} \cdot A \cdot \frac{E}{6\pi\eta r_i} \tag{8.61}$$

This equation shows that the ionic current is related to the square of the charge on the ion. For virtually all ionic solutions, the ionic currents of the positive and negative ions I_+ and I_- will be different. In order to maintain overall electrical neutrality, the oppositely charged ions have to move at different velocities.

Finally, the basic relationship between the voltage V across a conductor and the current I flowing through the conductor is known as *Ohm's law*:

$$V \propto I \tag{8.62}$$

The proportionality constant is defined as the *resistance, R*, of the system:

$$V = IR$$

Measurements of the resistances of ionic solutions show that the resistance is directly proportional to the distance, ℓ, between two electrodes and inversely proportional to the area A of the electrodes (which usually are the same size):

$$R = \rho \cdot \frac{\ell}{A} \tag{8.63}$$

The proportionality constant ρ is called the *specific resistance* or the *resistivity* of the solution, and has units of ohm·meter or ohm·cm. We also define the *conductivity* κ (also called the *specific conductance*) as the reciprocal of the resistivity:

$$\kappa = \frac{1}{\rho} \tag{8.64}$$

Conductivities have units of $\text{ohm}^{-1}\cdot\text{m}^{-1}$.* Resistivities or conductivities are extremely easy to measure experimentally using modern electrical equipment. However, as one might expect, they are quite variable because ρ would depend not only on the charge on the ions but on the concentration of the solution. It is better to define a quantity that takes these factors into account. The *equivalent conductance* of an ionic solute, Λ, is defined as

$$\Lambda = \frac{\kappa}{N} \tag{8.65}$$

where N is the normality of the solution (Λ is the capital Greek letter lambda). Recall that *normality* is defined in terms of number of equivalents per liter of solution. The use of equivalents rather than moles takes ionic charge into account.

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*The unit *siemen* (abbreviated S) is defined as ohm^{-1}, so conductivity values are sometimes given in units of S/m.

Table 8.4 Some values of Λ_0 for ionic salts

Salt	**Λ_0 (cm^2/normal·ohm)**
NaCl	126.45
KCl	149.86
KBr	151.9
NH_4Cl	149.7
$CaCl_2$	135.84
$NaNO_3$	121.55
KNO_3	144.96
$Ca(NO_3)_2$	130.94
HCl	426.16
LiCl	115.03
$BaCl_2$	139.98

Again, as expected, the equivalent conductance changes with concentration. However, it was noted by early investigators that for dilute (less than about 0.1 normal) solutions, Λ varied with the square root of the concentration, and the y-intercept of the straight line of Λ versus $\sqrt{N}$ was a value of Λ that was characteristic of the ionic solute. This characteristic, infinitely diluted value is given the symbol Λ_0. Various values of Λ_0 are listed in Table 8.4. Mathematically, the relationship between the equivalent conductance versus concentration can be expressed as

$$\Lambda = \Lambda_0 + K \cdot \sqrt{N} \tag{8.66}$$

where K is a proportionality constant that relates the slope of the straight line. Equation 8.66 is called *Kohlrausch's law* after Friedrich Kohlrausch, a German chemist who first proposed it in the late 1800s after a detailed study of the electrical properties of ionic solutions. Debye and Hückel, and later the Norwegian chemist Lars Onsäger, derived an expression for K:

$$K = -(60.32 + 0.2289\Lambda_0) \tag{8.67}$$

When combined, equations 8.66 and 8.67 are called the *Onsäger equation* for the conductance of ionic solutions.

8.9 Summary

Ions play a key role in many thermodynamic systems. Because ionic solutions can carry a current, chemical changes not considered in previous chapters might occur spontaneously. Some of those changes are very useful, because we can extract electrical work from those systems. Some of these changes are spontaneous but not inherently useful. For example, corrosion is one electrochemical process that is by definition an undesirable process. We can undo or reverse these undesirable processes, of course—but the second law of thermodynamics says that each of those processes will be inefficient to some degree. The laws of thermodynamics do allow us to determine how much energy we can get from (or must put into) a process, and we have been able to define standard electrochemical potentials to aid in those calculations.

The application of thermodynamics to electrochemical systems also helps us understand potentials at nonstandard conditions and gives us a relationship with the equilibrium constant and reaction quotient. However, we understand now that concentration is not necessarily the best unit to relate to the properties of a solution. Rather, activity of ions is a better unit to use. Using Debye-Hückel theory, we have ways of calculating the activities of ions so we can more precisely model the behavior of nonideal solutions.

8.2 Charges

8.1. What is the charge on a small sphere that is attracted to another sphere having charge 1.00 C if the spheres are 100.0 m apart and the force of attraction is 0.0225 N?

8.2. The force of attraction due to gravity follows an equation similar to Coulomb's law:

$$F = G \cdot \frac{m_1 \cdot m_2}{r^2}$$

where m_1 and m_2 are the masses of the objects, r is the distance between the objects, and G is the gravitational constant, which equals 6.672×10^{-11} $\text{N·m}^2/\text{kg}^2$.

(a) Calculate the force of gravitational attraction between Earth and the sun if the mass of Earth equals 5.97×10^{24} kg, the mass of the sun is 1.984×10^{30} kg, and the average distance between them is 1.494×10^8 km.

(b) Assuming that the sun and Earth would have the same magnitude but opposite charges, what charge is necessary to provide a coulombic force that equals the gravitational force between the sun and Earth? How many moles of electrons is that? To put your answer in perspective, consider that if Earth were composed of pure iron, it would contain about 10^{26} moles of Fe atoms.

8.3. Two small metallic bodies are given opposite charges, with the negatively charged body having twice the charge of the positively charged body. They are immersed in water (dielectric constant = 78) at a distance of 6.075 cm, and it is found that the force of attraction between the two metal pieces is 1.55×10^{-6} N. **(a)** What are the charges on the pieces of metal? **(b)** What are the electric fields of the two bodies?

8.4. In the centimeter-gram-second (cgs) system of units, a statcoulomb is a unit of charge such that $(1\ \text{statcoulomb})^2/(1\ \text{cm})^2 = 1$ dyne, the cgs unit of force. How many statcoulombs are there in a coulomb?

8.5. What is the force of attraction between a negatively charged electron and a positively charged proton at a distance of 0.529 Å? You will need to look up the charge on the electron and proton (which have the same magnitude but opposite sign charges), and use the fact that $1\ \text{Å} = 10^{-10}$ m.

8.3 & 8.4 Energy, Work, and Standard Potentials

8.6. How much work is required to move a single electron through a constant electric field of 1.00 V? (This amount of work, or energy, is defined as an *electron volt.*)

8.7. Explain why an electromotive force is *not,* in fact, a force.

8.8. Explain why $E^\circ_{1/2}$ values are not necessarily strictly additive. (*Hint:* consider the properties of intensive and extensive variables.)

8.9. For each of the following reactions, determine the overall balanced electrochemical reaction, its standard electric potential, and the standard Gibbs free energy of the reaction. You may have to add solvent molecules (that is, H_2O) to balance the reactions. Consult Table 8.2 for the half-reactions.

(a) $MnO_2 + O_2 \rightarrow OH^- + MnO_4{}^-$

(b) $Cu^+ \rightarrow Cu + Cu^{2+}$

(c) $Br_2 + F^- \rightarrow Br^- + F_2$

(d) $H_2O_2 + H^+ + Cl^- \rightarrow H_2O + Cl_2$

8.10. On the left side of equation 8.21, ΔG° is extensive (that is, dependent on amount) whereas on the right side of equation 8.21, E° is intensive (that is, independent of amount). Explain how the intensive variable can be related to the extensive variable.

8.11. Is the disproportionation reaction $Fe^{2+} \rightarrow Fe + Fe^{3+}$ spontaneous? What is ΔG° for the reaction?

8.12. A process requires 5.00×10^2 kJ of work to be performed. Which of the following reactions might be used to provide that work?

(a) $Zn\ (s) + Cu^{2+} \rightarrow Zn^{2+} + Cu\ (s)$

(b) $Ca\ (s) + H^+ \rightarrow Ca^{2+} + H_2$

(c) $Li\ (s) + H_2O \rightarrow Li^+ + H_2 + OH^-$

(d) $H_2 + OH^- + Hg_2Cl_2 \rightarrow H_2O + Hg + Cl^-$

8.13. If a calomel electrode is used instead of a standard hydrogen electrode, are the E° values shifted *up* or *down* by 0.2682 V? Justify your answer by determining the voltages of the spontaneous electrochemical reactions of each standard electrode with the half-reactions $Li^+ + e^- \rightarrow Li\ (s)$ and with $Ag^+ + e^- \rightarrow Ag$.

8.14. Determine E° and ΔG for each of the following reactions.

(a) $Au^{3+}\ {}^+\ 2e^- \rightarrow Au^+$

(b) $Sn^{4+} + 4e^- \rightarrow Sn$

8.15. Conventional chemical wisdom states that metallic elements are more reactive on the lower left side of the periodic table, and nonmetallic elements are more reactive on the upper right side of the periodic table. Electrochemically, this suggests that fluorine and cesium would have the extreme values of E°. Fluorine does have a very positive E° with respect to the SHE, at 2.87 V. However, lithium has one of the highest E° values for a metal, at −3.045 V. (Cesium's is only −2.92 V.) Can you explain this?

8.16. Under biochemical standard states, the potential for the reaction

$$NAD^+ + H^+ + 2e^- \longrightarrow NADH$$

is −0.320 V. If the concentrations of NAD^+ and NADH are 1.0 M, what is the concentration of H^+ under these conditions? See the end of section 8.4 for E° for this reaction.

8.5 Nonstandard Potentials and Equilibrium Constants

8.17. What is the $Zn^{2+}:Cu^{2+}$ ratio on a Daniell cell that has a voltage of 1.000 V at 25.0°C? Can you say what the individual concentrations of Zn^{2+} and Cu^{2+} are? Why or why not?

8.18. The thermite reaction can act as the basis of an electrochemical cell:

$$2Al\ (s) + Fe_2O_3\ (s) \longrightarrow Al_2O_3\ (s) + 2Fe\ (s)$$

Estimate the electrochemical potential of this reaction at 1700°C if $E°$ is 1.625 V. You will need to look up thermodynamic data in Appendix 2.

8.19. A *concentration cell* has different concentrations of the same ions, but because of the different concentrations there is a very small voltage between the cells. This effect is especially problematic for corrosion. Consider the following overall reaction, which is assumed to occur in the presence of metallic iron:

$$Fe^{3+}\ (0.08\ M) \longrightarrow Fe^{3+}\ (0.001\ M)$$

(a) What is $E°$?

(b) What is the expression for Q?

(c) What is E for the concentration cell?

(d) Should concentration cells be considered another type of colligative property? Explain your answer.

8.20. (a) What is the equilibrium constant for the following reaction?

$$H_2 + 2D^+ \rightleftharpoons D_2 + 2H^+$$

$E°$ for $2D^+ + 2e^- \rightarrow D_2$ is -0.044 V. **(b)** Based on your answer, which isotope of hydrogen prefers to be in the +1 state in aqueous solution?

8.21. Estimate the temperature needed for the reaction in exercise 8.20 to have an $E°$ of 0.00 V. Assume that $S[D^+(aq)] \approx 0$.

8.22. Redo Example 8.5 by correcting the entropies for temperature from 298 K to 500 K using the appropriate thermodynamic equations. By how much does the final answer differ?

8.23. Determine an expression for $\Delta C_p°$, the change in the constant-pressure heat capacity, for an electrochemical process. *Hint:* see equation 8.30 and use the definition of heat capacity.

8.24. Derive equation 8.33.

8.25. Determine E for the concentration cell whose net reaction is $Cu^{2+}\ (0.035\ m) \rightarrow Cu^{2+}\ (0.0077\ m)$.

8.26. Determine the ratio of molarities necessary to have E equal to 0.050 V for a concentration cell composed of **(a)** Fe^{2+} ions; **(b)** Fe^{3+} ions; **(c)** Co^{2+} ions. **(d)** Compare your answers and explain the differences or similarities.

8.27. Determine K_{sp} for AgCl using electrochemical data.

8.28. What is the solubility product constant of Hg_2Cl_2, which dissociates into ${Hg_2}^{2+}$ and Cl^- ions?

8.29. What is the pH of a hydrogen ion solution if an H electrode is connected to a ${MnO_4}^-/Mn^{2+}$ half cell with $[{MnO_4}^-] = 0.034\ m$ and $[Mn^{2+}] = 0.288\ m$? $E = 1.200$ V. Assume $p_{H_2} = 1$ bar. See Table 8.2 for $E°$ data.

8.30. Using the cell from Example 8.8, determine whether the oxidation of Fe (the major reaction in the corrosion of iron) to Fe^{2+} is promoted by high pH (basic solutions) or low pH (acidic solutions).

8.31. What is the equilibrium concentration of Cl^- in a standard calomel electrode? (*Hint:* you will need to determine the K_{sp} for Hg_2Cl_2.)

8.6 & 8.7 Ions in Solution; Debye-Hückel Theory

8.32. Show that $a_\pm$ can be written as $\gamma_\pm^{n_+} \cdot m^{n_\pm} \cdot n_+^{n_+} \cdot n_-^{n_-}$, where m is the original molality of the ionic solution.

8.33. Determine ionic strengths for the following solutions. Assume that they are 100% ionized. **(a)** 0.0055 molal HCl, **(b)** 0.075 molal $NaHCO_3$, **(c)** 0.0250 molal $Fe(NO_3)_2$, **(d)** 0.0250 $Fe(NO_3)_3$

8.34. Although it is not an ionic solute, a 1.00-molal solution of ammonia, NH_3, is actually a weak electrolyte and has an ionic strength of about 1.4×10^{-5} molal. Explain.

8.35. Calculate the molar enthalpy of formation of I^- (aq) if that of $H_2\ (g) + I_2\ (s) \rightarrow 2H^+\ (aq) + 2I^-\ (aq)$ is -110.38 kJ.

8.36. The entropy of formation of Mg^{2+} (aq) is -138.1 J/mol·K. Explain **(a)** why this value doesn't violate the third law of thermodynamics, and **(b)** from a molecular level, why the entropy of formation of *any* ion might be negative.

8.37. Hydrofluoric acid, HF (aq), is a weak acid that is not completely dissociated in solution.

(a) Using the thermodynamic data in Appendix 2, determine $\Delta H°$, $\Delta S°$, and $\Delta G°$ for the dissociation process.

(b) Calculate the acid dissociation constant, K_a, for HF (aq) at 25°C. Compare it to a handbook value of 3.5×10^{-4}.

8.38. Determine $\Delta H°$, $\Delta S°$, and $\Delta G°$ for the dissolution reactions for $NaHCO_3$ and Na_2CO_3. (See Appendix 2 for data.)

8.39. Verify the value and unit for equation 8.54.

8.40. The mean activity coefficient for an aqueous 0.0020-molal solution of KCl at 25°C is 0.951. How well does the Debye-Hückel limiting law, equation 8.50, predict this coefficient? As an additional exercise, calculate γ using equations 8.52 and 8.53 [where $å\ (K^+) = 3 \times 10^{-10}$ m and $å\ (Cl^-) = 3 \times 10^{-10}$ m] and $\gamma_\pm$ using equation 8.44.

8.41. Human blood plasma is approximately 0.9% NaCl. What is the ionic strength of blood plasma?

8.42. Approximate the expected voltage for the following electrochemical reaction using **(a)** the given molal concentrations and **(b)** the calculated activities using simple Debye-Hückel theory. The value of å for both Zn^{2+} and Cu^{2+} is 6×10^{-10} m.

$$\text{Zn (s)} + \text{Cu}^{2+} \text{(aq, 0.05 molal)} \longrightarrow \text{Zn}^{2+} \text{(aq, 0.1 molal)} + \text{Cu (s)}$$

Explain why you get the answers you do.

8.43. **(a)** Explain why it is important to specify an identity of the anion in Example 8.12 even though it is a spectator ion.

(b) Recalculate part b of Example 8.12, assuming that the salts are both sulfate salts rather than nitrate salts. Consider the concentrations given in the example as the resultant *cation* concentration, not the concentration of the salt itself.

8.44. Is equation 8.40 supported by Table 8.3? Explain your answer.

8.8 Transport and Conductance

8.45. Show that equation 8.61 gives units of amperes, a unit of current. You will have to use equation 8.5 to get proper units for the electric field *E*.

8.46. (a) The salt $NaNO_3$ can be thought of as $NaCl + KNO_3 - KCl$. Demonstrate that Λ_0 values show this type of additivity by calculating Λ_0 for $NaNO_3$ from the Λ_0 values of NaCl, KNO_3, and KCl found in Table 8.4. Compare your calculated value with the Λ_0 value for $NaNO_3$ in the table. **(b)** Predict approximate Λ_0 values for NH_4NO_3 and $CaBr_2$ using the values given in Table 8.4.

8.47. In a galvanic cell, determine whether I_+ and I_- are moving toward the cathode or the anode. How about for an electrolytic cell?

8.48. What is the estimated velocity for Cu^{2+} ions moving through water in a Daniell cell in which the electric field is 100.0 V/m? Assume that å for Cu^{2+} is 4 Å and the viscosity of water is 0.00894 poise. Comment on the magnitude of your answer.

Symbolic Math Exercises

8.49. Set up an expression that evaluates the force on two unit charges of opposite sign at varying distance in vacuum and in a medium having some dielectric constant ϵ_r. Then, evaluate the force between the two charges at distances ranging from 1 Å to 25 Å in 1-Å increments. How do the values vary between a vacuum and some medium with a nonzero dielectric constant? Do the same evaluations for charges of same sign, and compare the results with charges of opposite sign.

8.50. A Daniell cell is constructed with all standard concentrations except for Zn^{2+}. The concentration of the zinc ion has values of 0.00010 M, 0.0074 M, 0.0098 M, 0.0275 M, and 0.0855 M. What are the *E* values of the cell? What trend do the *E* values show?

8.51. Ionic salts are composed of ions that can have charges of up to 4+ and 3−. Construct a table of ionic strengths that tabulate *I* versus ion charge for every possible combination, assuming a 1-molal solution of each salt.

8.52. Calculate **(a)** the solubility product constant for Ag_2CO_3 and **(b)** the value for K_w using the following data:

$$\text{Ag}_2\text{CO}_3 \text{ (s)} + 2e^- \longrightarrow 2\text{Ag (s)} + \text{CO}_3{}^{2-} \text{ (aq)} \qquad E_{1/2} = 0.47 \text{ V}$$

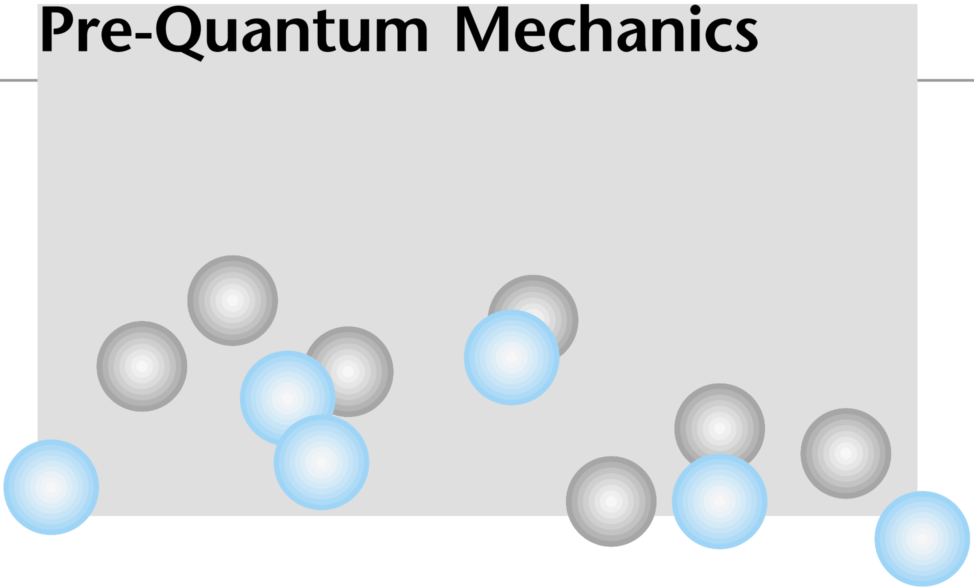
$$\text{Ag}^+ \text{ (aq)} + e^- \longrightarrow \text{Ag (s)} \qquad E_{1/2} = 0.7996 \text{ V}$$

$$\text{O}_2 \text{ (g)} + 2\text{H}_2\text{O } (\ell) + 4e^- \longrightarrow 4\text{OH}^- \text{ (aq)} \qquad E_{1/2} = 0.401 \text{ V}$$

$$\text{O}_2 \text{ (g)} + 4\text{H}^+ \text{ (aq)} + 4e^- \longrightarrow 2\text{H}_2\text{O } (\ell) \qquad E_{1/2} = 1.229 \text{ V}$$

9

Pre-Quantum Mechanics



AS SCIENCE HAS MATURED, it has developed the perspective that the physical world is regular and that its behavior follows certain rules and guidelines. By the 1800s, chief among these rules were the laws of mechanics that explained the motion of bodies of matter; specifically, Newton's three laws of motion. Scientists felt confident that they were beginning to understand the natural world and how it worked.

Early in the 1800s, and certainly by the middle and end of the century, however, little hints began to appear suggesting that scientists really didn't understand what was going on. Or, rather, that the accepted physical laws neither applied to nor predicted certain events. Toward the end of the nineteenth century, it was obvious to a few radical thinkers that a new theory describing the behavior of matter would be necessary in order to understand the nature of the universe. Finally, in 1925–1926, a new theory named quantum mechanics was shown to accurately account for the new observations that did not fit with the earlier, classical mechanics.

In order to fully appreciate quantum mechanics and what it provides for chemists, it is crucial to review the state of physical science immediately before quantum mechanics. In this chapter, we review classical mechanics and discuss the phenomena that classical mechanics did not explain. Although it may not seem like chemistry at first, remember that a major goal in physical chemistry is *to model the behavior of atoms and molecules*. Since the chemically most important parts of the atom are the electrons, a proper understanding of electron behavior is absolutely necessary to any understanding of chemistry. Because the electron had been shown to be a piece of matter, classical scientists tried to use classical equations of motion to understand the behavior of the electron. However, they soon discovered that the old models didn't work for such a small piece of matter. A new model had to be developed, and quantum mechanics was that model.

9.1 Synopsis

In this chapter, we start with a review of how scientists classify the behavior of the motion of matter. There are several mathematical ways to describe motion, Newton's laws being the most common. A quick historical review shows that several phenomena could not be explained by the scientific thinking of the 1800s. Most of these phenomena were based on the properties of atoms that were only then being examined directly. These phenomena are described here because they will be considered later in light of new theories such as quantum mechanics. Of course, since most matter is ultimately studied using light, a proper understanding of the nature of light is necessary. This understanding began to change dramatically with Planck and his quantum theory of blackbodies. Proposed in 1900, quantum theory opened a new age of science in which new ideas began replacing the old ones—not because of lack of application (classical mechanics is still a very useful topic), but because these old ideas lacked the subtlety to explain newly observed phenomena properly. Einstein's application of quantum theory to light in 1905 was a crucial step. Finally, Bohr's theory of hydrogen, de Broglie's matter waves, and other new ideas set the stage for the introduction of modern quantum mechanics.

9.2 Laws of Motion

Throughout the Middle Ages and the Renaissance, natural philosophers studied the world around them and tried to understand the universe. Foremost among these natural philosophers was Isaac Newton (Figure 9.1), who in the late 1600s and early 1700s deduced several statements that summarize the motion of bodies of matter. We know them as *Newton's laws of motion.*

Briefly, they are:

- *The first law of motion:* An object at rest tends to stay at rest, and an object in motion tends to stay in motion, as long as no unbalanced force acts on that object. (This is sometimes known as the law of inertia.)
- *The second law of motion:* If an unbalanced force acts on an object, that object will accelerate in the direction of the force, and the amount of acceleration will be inversely proportional to the mass of the object and directly proportional to the force.
- *The third law of motion:* For every action, there is an equal and opposite reaction.


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Figure 9.1 Sir Isaac Newton (1642–1727). In 1687, he published *Principia Mathematica,* in which his three laws of motion were first stated. They are still the most widespread way to describe the motion of objects. Knighted in 1705, Newton received this honor not for his scientific achievements, as is usually assumed, but for his political activities.

Newton's second law should be considered more closely, since it is perhaps the most familiar of the laws. Force, **F**, is a *vector* quantity, having magnitude and direction. For a single object of mass *m*, Newton's second law is usually expressed in the form*

$$\mathbf{F} = m\mathbf{a} \tag{9.1}$$

where the boldfaced variables are vector quantities. Note that the acceleration **a** is also a vector, since it too has magnitude and direction. Typical units for mass, acceleration, and force are kg, m/s^2, and newton (where 1 N = 1 kg·m/s^2). Equation 9.1 assumes that mass is constant.

Equation 9.1 can be written in a different way using the symbolism of calculus. Acceleration is the change of the velocity vector with respect to time, or $d\mathbf{v}/dt$. But velocity **v** is the change in position with respect to time. If we represent the position by its one-dimensional coordinate **x**, then we can write acceleration as the time derivative of the time derivative of position, or

$$\mathbf{a} = \frac{d^2\mathbf{x}}{dt^2} \tag{9.2}$$

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*Its most general form is $\mathbf{F} = dp/dt = dm\mathbf{v}/dt$, but the form in equation 9.1 is probably the most common way to express Newton's second law.

This means that Newton's second law can be written

$$\mathbf{F} = m\frac{d^2\mathbf{x}}{dt^2} \tag{9.3}$$

It is not uncommon to ignore the vector character of force and position and express equation 9.3 as

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

Note two things about Newton's second law. First, it is a second-order ordinary differential equation.[†] This means that in order to understand the motion of any object in general, we must be willing and able to solve a second-order differential equation. Second, since position is also a vector, when we consider changes in position or velocity or acceleration we are not only concerned about changes in the magnitude of these values but changes in their *direction*. A change in direction constitutes an acceleration since the velocity, a vector quantity, is changing its direction. This idea has serious consequences in the consideration of atomic structure, as we will see later.

Though they took time to be accepted by contemporary scientists, Newton's three laws of motion dramatically simplified the understanding of objects in motion. Once these statements were accepted, simple motion could be studied in terms of these three laws. Also, the behavior of objects as they moved could be predicted, and other properties such as momentum and energies could be studied. When forces such as gravity and friction were better understood, it came to be realized that Newton's laws of motion properly explained the motion of *all* bodies. From the seventeenth through the nineteenth centuries, the vast applicability of Newton's laws of motion to the study of matter convinced scientists that all motion of all physical bodies could be modeled on those three laws.

There is always more than one way to model the behavior of an object. It is just that some ways are easier to understand or apply than others. Thus, Newton's laws are not the only way of expressing the motion of bodies. Lagrange and Hamilton each found different ways of modeling the motion of bodies. In both cases the mathematics of expressing the motion are different, but they are mathematically equivalent to Newton's laws.

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Figure 9.2 Joseph Louis Lagrange (1736–1813). Lagrange reformulated Newton's laws in a different but equivalent way. Lagrange was also an astronomer of some repute. In 1795, he and several other prominent French scientists devised the metric system.

Joseph Louis Lagrange, a French-Italian mathematician and astronomer (Figure 9.2), lived a hundred years after Newton. By this time the genius of Newton's contributions had been recognized. However, Lagrange was able to make his own contribution by rewriting Newton's second law in a different but equivalent way.

If the kinetic energy of a particle of mass m is due solely to the velocity of the particle (a very good assumption at that time), then the kinetic energy K is

$$K = \frac{m}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) \tag{9.4}$$

where $\dot{x} = dx/dt$, and so on. (It is a standard notation to use a dot over a variable to indicate a derivative with respect to time. Two dots indicates a second

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[†] Recall that an ordinary differential equation (ODE) has only ordinary, but not partial, differentials, and that the order of an ODE is the highest order of the differentials in the equation. For equation 9.3, the second derivative indicates a second-order ODE.

derivative with respect to time, and so on). Further, if the potential energy V is a function only of position, that is, the coordinates x, y, and z:

$$V = V(x, y, z) \tag{9.5}$$

then the *Lagrangian function* L (or simply "the Lagrangian") of the particle is defined as

$$L(\dot{x}, \dot{y}, \dot{z}, x, y, z) = K(\dot{x}, \dot{y}, \dot{z}) - V(x, y, z) \tag{9.6}$$

L has units of joules, which is the SI unit of energy. ($1\ \text{J} = 1\ \text{N}\cdot\text{m} = 1\ \text{kg}\cdot\text{m}^2/\text{s}^2$)[‡] Understanding that the coordinates x, y, and z are independent of each other, one can now rewrite Newton's second law in the form of Lagrange's equations of motion:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) = \frac{\partial L}{\partial x} \tag{9.7}$$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{y}}\right) = \frac{\partial L}{\partial y} \tag{9.8}$$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{z}}\right) = \frac{\partial L}{\partial z} \tag{9.9}$$

We are using partial derivatives here, because L depends on several variables. One of the points to notice about the laws of motion equations (9.7–9.9) is that the equations have exactly the same form regardless of the coordinate. One can show that this holds true for any coordinate system, like the spherical polar coordinate system in terms of r, φ, and θ that we will use later in our discussion of atoms.

Lagrange's equations, mathematically equivalent to Newton's equations, rely on being able to define the kinetic and potential energy of a system rather than the forces acting on the system. Depending on the system, Lagrange's differential equations of motion can be easier to solve and understand than Newton's differential equations of motion. (For example, systems involving rotation about a center, like planets about a sun or charged particles about an oppositely charged particle, are more easily described by the Lagrangian function because the equation that describes the potential energy is known.)

Irish mathematician Sir William Rowan Hamilton was born in 1805, eight years before the death of Lagrange. Hamilton (Figure 9.3) also came up with a different but mathematically equivalent way of expressing the behavior of matter in motion. His equations are based on the Lagrangian and they assume that, for each particle in the system, L is defined by three time-dependent coordinates $\dot{q}_j$, where $j = 1, 2,$ or 3. (For example, they might be $\dot{x}$, $\dot{y}$, or $\dot{z}$ for a particle having a certain mass.) Hamilton defined three *conjugate momenta* for each particle, p_j, such that

$$p_j = \frac{\partial L}{\partial \dot{q}_j}, \qquad j = 1, 2, 3 \tag{9.10}$$

The *Hamiltonian function* ("the Hamiltonian") is defined as

$$H(p_1, p_2, p_3, q_1, q_2, q_3) = \left(\sum_{j=1}^{3} p_j \cdot \dot{q}_j\right) - L \tag{9.11}$$

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Figure 9.3 Sir William Rowan Hamilton (1805–1865). Hamilton reformulated the law of motion of Newton and Lagrange into a form that ultimately provided a mathematical basis for modern quantum mechanics. He also invented matrix algebra.

[‡] Equations 9.4 and 9.5 embody the definitions of kinetic and potential energies: kinetic energy is energy of motion, and potential energy is energy of position.

The utility of the Hamiltonian function depends on the kinetic energy K, which is a function of the time derivatives of position, that is, the velocities. If K were to depend on the sum of the *square* of velocities:

$$K = \sum_{j=1}^{N} c_j \dot{q}_j^2 \qquad \textbf{(9.12)}$$

(where the c_j values are the expansion coefficients of the individual components of K) then it can be shown that the Hamiltonian function is

$$H = K + V \qquad \textbf{(9.13)}$$

That is, H is simply the sum of the kinetic and potential energies. The kinetic energy expressions that we consider here are indeed of the form in equation 9.12. The Hamiltonian function conveniently gives the *total energy of the system,* a quantity of fundamental importance to scientists. The Hamiltonian function can be differentiated and separated to show that

$$\frac{\partial H}{\partial p_j} = \dot{q}_j \qquad \textbf{(9.14)}$$

$$\frac{\partial H}{\partial q_j} = -\dot{p}_j \qquad \textbf{(9.15)}$$

These last two equations are Hamilton's equations of motion. There are two equations for each of the three spatial dimensions. For one particle in three dimensions, equations 9.14 and 9.15 give six first-order differential equations that need to be solved in order to understand the behavior of the particle. Both Newton's equations and Lagrange's equations require the solution of three second-order differential equations for each particle, so that the amount of calculus required to understand the system is the same. The only difference lies in what information one knows to model the system or what information one wants to get about the system. This determines which set of equations to use. Otherwise, they are all mathematically equivalent.

Example 9.1

Show that, for a simple one-dimensional Hooke's-law harmonic oscillator having mass m, the three equations of motion yield the same results.

Solution

For a Hooke's-law harmonic oscillator, the (nonvector) force is given by

$$F = -kx$$

and the potential energy is given by

$$V = \tfrac{1}{2}kx^2$$

where k is the force constant.

a. From Newton's laws, a body in motion must obey the equation

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

and the two expressions for force can be equated to give

$$m\frac{d^2x}{dt^2} = -kx$$

which can be rearranged algebraically to yield the second-order differential equation

$$\frac{d^2x}{dt^2} + \frac{k}{m}x = 0$$

This differential equation has the general solution $x(t) = A \sin \omega t + B \cos \omega t$, where A and B are constants characteristic of the particular system (determined, for example, by the initial position and velocity of the oscillator) and

$$\omega = \left(\frac{k}{m}\right)^{1/2}$$

b. For Lagrange's equations of motion, we need the kinetic energy K and the potential energy V. Both are the classical expressions

$$K = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2 = \frac{1}{2}m\dot{x}^2$$

$$V = \frac{1}{2}kx^2$$

The Lagrangian function L is thus

$$L = \frac{1}{2}m\dot{x}^2 - \frac{1}{2}kx^2$$

The Lagrange equation of motion for this one-dimensional system is

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) - \frac{\partial L}{\partial x} = 0$$

where equation 9.7 has been rewritten to equal zero. Recalling that $\dot{x}$ is the derivative of x with respect to time, we can take the derivative of L with respect to $\dot{x}$ as well as the derivative of L with respect to x. We find that

$$\frac{\partial L}{\partial \dot{x}} = m\dot{x} \qquad \frac{\partial L}{\partial x} = -kx$$

Substituting these expressions into the Lagrange equation of motion, we get

$$\frac{d}{dt}(m\dot{x}) + kx = 0$$

Since mass does not change with time, the derivative with respect to time affects only $\dot{x}$. This expression then becomes

$$m\frac{d}{dt}(\dot{x}) + kx = 0$$

which can be rearranged as

$$\frac{d^2x}{dt^2} + \frac{k}{m}x = 0$$

This is the exact same second-order differential equation found using Newton's equations of motion. It therefore has the same solutions.

c. For Hamilton's equation of motion, in this example the general coordinate q is simply x, and $\dot{q}$ equals $\dot{x}$. We need to find the momentum as defined by equation 9.10. It is

$$p = m\dot{x}$$

Since we are confining motion to one dimension, only one momentum needs to be defined. Using the Lagrangian defined above, we can substitute into the one-dimensional Hamiltonian

$$H = p \cdot \dot{x} - L$$

(See equation 9.11.) Substituting for p and L:

$$H = m\dot{x} \cdot \dot{x} - \left(\tfrac{1}{2}m\dot{x}^2 - \tfrac{1}{2}kx^2\right)$$

$$= \tfrac{1}{2}m\dot{x}^2 + \tfrac{1}{2}kx^2$$

where in the last equation we have combined the first two terms. Because we will need to solve the differential equations given by equations 9.14 and 9.15, it will be easier for the first derivative if we rewrite the Hamiltonian as

$$H = \frac{1}{2m}p^2 + \frac{1}{2}kx^2$$

Applying equation 9.14 to this expression, we get

$$\frac{\partial H}{\partial p} = 2\left(\frac{1}{2m}\right)p = \frac{1}{m}m\dot{x} = \dot{x}$$

which is what this derivative should be. We have not gotten anything new out of this expression. However, upon evaluating the derivative in 9.15 using the rewritten form of the Hamiltonian, we find:

$$\frac{\partial H}{\partial x} = kx$$

which, by equation 9.15, must equal $-\dot{p}$:

$$kx = -\dot{p}$$

or

$$kx = -\frac{d}{dt}p$$

$$kx = -\frac{d}{dt}m\dot{x}$$

$$kx = -m\frac{d^2x}{dt^2}$$

This can be rewritten as

$$\frac{d^2x}{dt^2} + \frac{k}{m}x = 0$$

which is the same differential equation that we found upon applying both Newton's and Lagrange's equations of motion.

Example 9.1 illustrates that the three different equations of motion produce the same description for the motion of a system, only by different routes. Why present three different ways of doing the same thing? Because all three ways are not equally easy to apply to all situations! Newton's laws are most popular for straight-line motion. However, for other systems (like systems involving revolution about a center) or when knowledge of the total energy of a system is important, the other forms are more appropriate to use. We will find later that for atomic and molecular systems, the Hamiltonian function is used almost exclusively.

Before we leave this topic, it is important to recognize what these equations of motion provided. If one could indeed specify the forces acting on a particle, or a group of particles, one could predict how those particles would behave. Or if one knows the exact form of the potential energy of the particles in the system, or if one wants to know what the total energy of the system is, one could still model the system. Nineteenth-century scientists were complacent in their feeling that if the proper mathematical expressions for the potential energy or forces were known, then the complete mechanical behavior of the system could be predicted. Newton's, Lagrange's, and Hamilton's equations endowed scientists with a feeling of certainty that they knew what was going on in the world.

But with what type of systems were they dealing? Macroscopic ones, like a brick, a metal ball, a piece of wood. Since Dalton had enunciated his version of the modern atomic theory, the objects of matter called atoms must follow the same equations of motion. After all, what were atoms but tiny, indivisible pieces of matter? Atoms should behave no differently than regular matter does and would certainly be expected to follow the same rules. However, even as the Hamiltonian function was introduced as a new way to describe the motion of matter, some scientists started looking a little more closely at matter. They could not explain what they saw.

9.3 Unexplainable Phenomena

As science developed and advanced, scientists began to study the universe around them in different and new ways. In several important instances, they were not able to explain what they observed using contemporary ideas. It seems easy in hindsight to suggest that new ideas would be necessary. However, at that point no phenomena had been observed that would not be understood using the known science of the time. One must also understand the nature of the people who did the work: educated in the shadow of an assumed understanding of nature, they *expected* that nature would follow these rules. When unusual experimental results were measured, explanations were attempted based on classical science. It soon became clear that classical science could not explain certain observations, and cannot even to this day. It remained the task of a new generation of scientists to understand and explain the phenomena (with several important exceptions, almost everyone involved in the development of quantum mechanics was relatively young).

The unexplained phenomena were the observation of atomic line spectra, the nuclear structure of the atom, the nature of light, and the photoelectric effect. Certain experimental observations in these areas did not conform to the expectations of classical mechanics. But to really see why a new mechanics was necessary, it is important to review each of these phenomena and understand why classical mechanics did not explain the observations.

9.4 Atomic Spectra

In 1860, the German chemist Robert Wilhelm Bunsen (of Bunsen burner fame) and the German physicist Gustav Robert Kirchhoff invented the spectroscope. This apparatus (Figure 9.4) used a prism to separate white light into

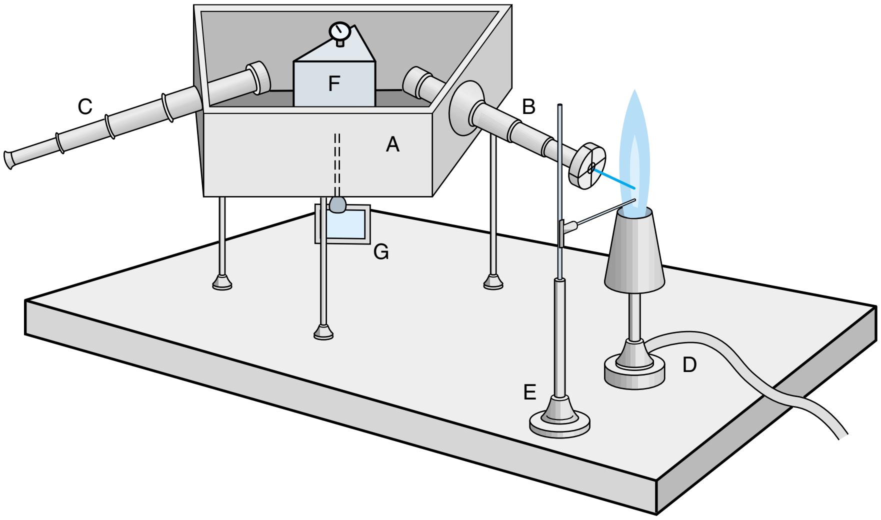

Figure 9.4 An example of an early spectroscope, like that invented by Bunsen and Kirchhoff. The two discovered several elements (cesium and rubidium among them) by detecting their characteristic light with a spectroscope. A. Spectrometer box. B. Input optics. C. Observing optics. D. Excitation source (Bunsen burner). E. Sample holder. F. Prism. G. Armature to rotate prism.

its component colors and pass this colored light through a chemical sample. The sample absorbed some wavelengths of light, not others, resulting in a dark line superimposed on a continuous spectrum of colors. Heated samples that gave off light would have this light analyzed through the spectroscope, showing only lines of light that appeared in the same relative positions as the dark lines. Bunsen and Kirchhoff eventually noticed that each element absorbed or emitted only characteristic wavelengths of light, and proposed that this might be a technique to identify the chemical elements. Figure 9.5 shows several characteristic spectra of some vapors of elements. Note that they are all different. In 1860, the proposal was put to the test by an analysis of a mineral whose spectrum showed new lines never before measured. Bunsen and Kirchhoff announced that the novel spectrum must be due to an undiscovered element. In this way, the element cesium was discovered, and its discovery was eventually confirmed by chemical analysis. In less than a year, rubidium was also discovered the same way.

Each element, then, had its characteristic spectrum, whether absorption (if light was passed through a gaseous sample of the element) or emission (if the

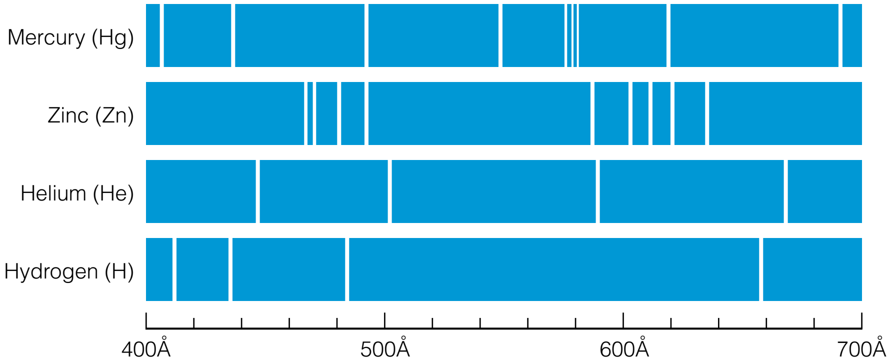

Figure 9.5 Line spectra of several elements. Note the relatively simple spectra for H and He.

sample was energetically stimulated so that it emitted light). Many of these spectra were complicated, but for some reason the spectrum of hydrogen was relatively simple (see Figure 9.5). Hydrogen was the lightest known element and probably the simplest, a fact that could hardly have been missed in the attempts to interpret its spectrum. In 1885, the Swiss mathematician Johann Jakob Balmer showed that the positions of the lines of light from hydrogen in the visible portion of the spectrum could be predicted by a simple arithmetic expression:

$$\frac{1}{\lambda} = R\left(\frac{1}{4} - \frac{1}{n^2}\right) \tag{9.16}$$

where λ is the wavelength of the light, n is an integer greater than 2, and R is some constant whose value is determined by measuring the wavelengths of the lines. The simplicity of the equation is startling, and it inspired other scientists to analyze the spectrum of hydrogen in other regions of the spectrum, like the infrared and ultraviolet regions. Although several other people (Lyman, Brackett, Paschen, Pfund) were to discover other simple progressions of lines in the hydrogen spectrum, in 1890 Johannes Robert Rydberg successfully generalized the progressions into a single formula:

$$\frac{1}{\lambda} \equiv \tilde{\nu} = R_{\mathrm{H}}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{9.17}$$

where n_1 and n_2 are different integers, n_2 *is less than* n_1, and R_{H} is known as the *Rydberg constant*. The variable $\tilde{\nu}$ is the wavenumber of the light and has units of inverse centimeters, or cm^{-1}, indicating the number of light waves per centimeter.* Interestingly enough, thanks to the precision with which the hydrogen atom spectrum can be measured, the Rydberg constant is one of the most accurately known physical constants: $109{,}737.315\ \mathrm{cm}^{-1}$.

Example 9.2

Determine the frequencies in cm^{-1} for the first three lines for the Brackett series of the hydrogen atom, where $n_2 = 4$.

Solution

If $n_2 = 4$, the first three lines in the Brackett series will have $n_1 = 5$, 6, and 7. Using equation 9.17 above and substituting for R_{H} and n_2, we get

$$\tilde{\nu} = 109{,}737.315\left(\frac{1}{4^2} - \frac{1}{n_1^2}\right)\ \mathrm{cm}^{-1}$$

Substituting 5, 6, and 7 for n_1 above, we calculate $2469\ \mathrm{cm}^{-1}$ ($n_1 = 5$), $3810\ \mathrm{cm}^{-1}$ ($n_1 = 6$), and $4619\ \mathrm{cm}^{-1}$ ($n_1 = 7$).

But the questions remained: Why was the hydrogen spectrum so simple? And why did Rydberg's equation work so well? Although it was tacitly understood that hydrogen was the lightest and simplest atom, there was absolutely no reason to assume that a sample of this matter would give off only certain wavelengths of light. It didn't matter that the spectra of other elements were a little more complicated and could not be described by any straightforward

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*The formal SI unit for wavenumber is m^{-1}, but quantities with cm^{-1} units are more common.

mathematical formula. The fact that the spectrum of hydrogen was so simple and so unexplainable caused a problem for classical mechanics. It turned out, about 30 years later, that classical mechanics could not explain it. Other theories were necessary.

9.5 Atomic Structure

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Figure 9.6 John Dalton (1766–1844). In 1803, Dalton restated the atomic theory of Democritus (fourth century B.C.) in a more modern form that with only slight modification is still considered valid today. In his honor, another name for an atomic mass unit is the dalton. Also in his honor, since he was the first person to write a description of color blindness, this affliction is sometimes referred to as daltonism. The original records of his experiments were destroyed by bombing in World War II.

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Figure 9.7 Sir Joseph John Thomson (1856–1940). Thomson is usually credited as the discoverer of the electron, although many people contributed to its identification as a basic building block of matter. Seven of his research assistants, who were also heavily involved in understanding the structure of matter, would eventually win Nobel Prizes.

In the fourth century B.C., Democritus suggested that matter was composed of tiny parts called atoms. However, experience suggests that matter is *smooth.* That is, it is continuous and not broken into individual pieces. Faced with mounting evidence, especially from the study of gases, John Dalton (Figure 9.6) revived the atomic theory in a modern version that gradually came to be accepted. Implicit in this theory was the idea that atoms are indivisible.

In the 1870s and 1880s, certain phenomena were investigated by passing an electrical current through an evacuated tube having a small quantity of gas in it. In the 1890s J. J. Thomson (Figure 9.7) performed a series of experiments in evacuated tubes and showed that the electrical discharge was not composed of electromagnetic radiation—mistakenly referred to as cathode rays—but was instead a stream of particles formed from some residual gas left in the tubes. Further, these particles had electric charges on them, indicated by a deflection of the stream by a magnetic field. Measurements of the charge-to-mass ratio, e/m, which could be measured by the amount of magnetic deflection of the stream, were extraordinarily high. This indicated either a huge charge or a tiny mass. Thomson speculated that the charge could not be large, leaving the tiny mass as the only possibility.

The mass of this particle, called the electron, had to be less than one-thousandth of that of a hydrogen atom (whose mass was known). But this indicated that some particles of matter are *smaller* than atoms, an idea that was supposedly precluded by the modern atomic theory. Obviously, this negatively charged particle was only a piece of an atom. The implication was that atoms were not indivisible.

Experiments by Robert Millikan between 1908 and 1917 established the approximate magnitude of the charge, which was then used with Thomson's e/m ratio to determine the mass of the electron. In his famous oil drop experiment, diagrammed in Figure 9.8, Millikan and coworkers introduced tiny oil droplets in between charged plates, subjected them to ionizing radiation (X rays), and varied the voltage over the plates to try to electrostatically levitate the drops. Knowing the density of the oil, the voltage difference between the plates, the radius of the droplets, and correcting for air buoyancy, Millikan calculated an approximate charge of 4.77×10^{-10} electrostatic units (esu) or about 1.601×10^{-19} coulombs (C). From the e/m, Millikan was able to calculate the mass of the electron as about 9.36×10^{-31} kg, about 1/1800 of the mass of a hydrogen atom. (The modern accepted value for the mass of an electron is 9.109×10^{-31} kg.) Since there are negatively charged particles in atoms, there should also be positively charged particles, so that matter would be electrically neutral. The proton, a positively charged particle, was identified by Ernest Rutherford in 1911.

Following Rutherford and Marsden's classic experiments with metal foil scattering in 1908, Rutherford proposed the nuclear model for atoms. In the nuclear model the majority of the mass—consisting of the protons and the later-discovered neutrons—is concentrated in a central region called the *nucleus,* and the smaller electrons revolve around the nucleus at some relatively great distance. The experiment and the resulting model are illustrated in Figure 9.9.

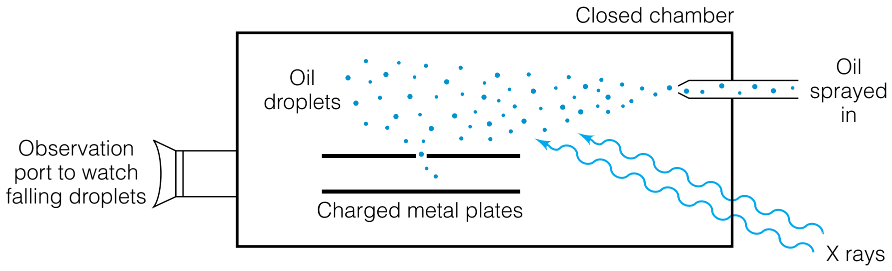

Figure 9.8 A representation of the Millikan oil drop experiment, in which the exact charge on the electron was determined. Using that information along with the charge-to-mass ratio (determined from experiments using magnets), the mass of the electron was determined to be much smaller than that of an atom. Dalton's atomic theory was not destroyed, just revised. An understanding of the behavior of the electron was the central focus of modern quantum mechanics.

Although the nuclear atom fit the dramatic results of the experiment, there was a major problem: According to Maxwell's electromagnetic theory, such an atom shouldn't be stable. (The equations of electrodynamics summarized by James Clerk Maxwell in the 1860s were another major advance in understanding nature.) Any time a charged particle is accelerated, any time it changes its speed *or direction* (since acceleration is a vector quantity), it should radiate energy. If an electron is attracted to a proton (and it was known then that opposite charges attract), it should accelerate toward the proton, and as it moves it should radiate energy. Eventually all of the energy of the particles should be radiated, they would have no energy, so the particles should collapse together and electrically neutralize each other. But they didn't.

If Maxwell's theory of electromagnetism, which worked so well with macroscopic bodies, also worked for atoms and subatomic particles, then electrons and protons—matter as we know it—shouldn't even exist! They would constantly be radiating energy, losing energy, and eventually collapsing together. But these investigators did not doubt the fact that matter was stable. The current theories of electromagnetism and classical mechanics simply did not explain the existence of atoms. Their very composition as separated charged particles flew in the face of the accepted understanding of the universe. (The eventual discovery of the uncharged neutron, announced by Chadwick in 1932, did not figure into this problem, since the neutron is electrically neutral.)

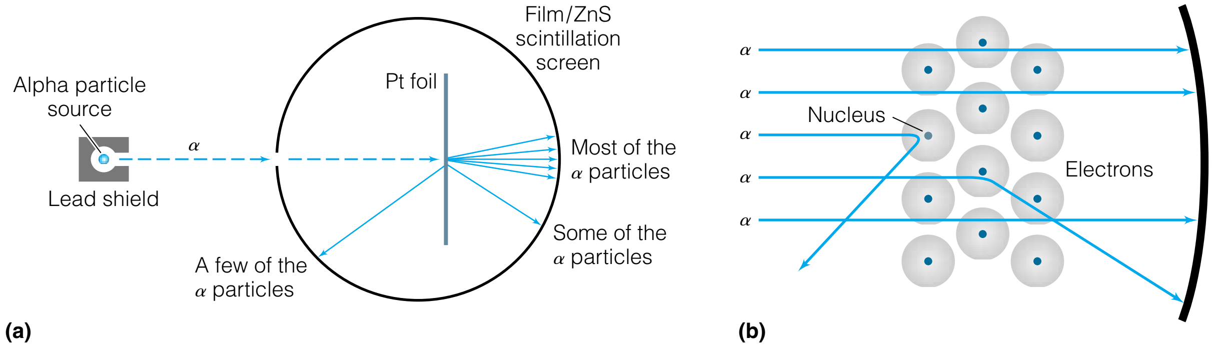

Figure 9.9 (a) A schematic of Rutherford and Marsden's experimental apparatus with platinum foil. (b) The nuclear model of the atom, based on the experiments. Three paths of alpha particles through the atom show how the alpha particles are influenced by a massive and heavily charged nucleus. Although some details of the model have been modified, the general idea remains intact: a massive nucleus with lighter electrons moving around it.

The study of radioactivity, beginning with Antoine-Henri Becquerel's discovery in 1896, was another problem relating to atomic structure. In fact, radioactivity was another enigma not explained by classical mechanics. Studies showed that atoms spontaneously gave off three distinct types of radiation, of which two were eventually shown to be particles of matter. The alpha particle (α) was identical to a doubly ionized helium atom, and the beta particle (β) was identical to an electron. [The third type of radiation, gamma (γ) radiation, is a form of electromagnetic radiation.] However, no known chemical process could eject particles from atoms in the manner indicated by radioactivity.

9.6 The Photoelectric Effect

In 1887 Heinrich Hertz, who is better known for his discovery of radio waves, noticed in his investigations of evacuated tubes that when light was shined on a piece of metal in a vacuum, various electrical effects were produced. Given that the electron was yet to be discovered, an explanation was not forthcoming. After the discovery of the electron, however, reinvestigation of this phenomenon by other scientists, especially the Hungarian-German physicist Philipp Eduard Anton von Lenard, indicated that the metals were indeed emitting electrons upon illumination. Ultraviolet light was the best light to use, and in a series of experiments several interesting trends were noticed. First, the frequency of light used to illuminate the metal made a difference. Below a certain frequency, called the *threshold frequency,* no electrons were given off; above that certain frequency, electrons were emitted. Second and more inexplicable, a greater intensity of light did not cause electrons to come off at greater speed, it increased the number of electrons that were emitted. However, a shorter wavelength (that is, a higher frequency) of light did cause the electrons to come off at greater speeds. This was unusual, for the modern theory of waves (especially sound waves) suggested that the intensity was directly related to the energy of the wave. Since light is a wave, a greater intensity of light should have a greater energy. The emitted electrons, however, did not come off at any greater kinetic energy when the intensity of the light was increased. The kinetic energy (equal to $\frac{1}{2}mv^2$) of the electrons did increase when the *frequency* of the light was increased. The current understanding of light, waves, and electrons did not supply any reasonable justification for these results.

9.7 The Nature of Light

Since the time of Newton, the question "What is light?" has been debated, mostly because of conflicting evidence. Some evidence showed that light acted as a particle, and some evidence indicated that light acted as a wave. However, Thomas Young's double-slit experiment in 1801 (Figure 9.10) demonstrated conclusively the diffraction patterns caused by constructive and destructive interference of light. It seemed clear that light was a wave of extremely small wavelength, about 4000–7000 Å depending on the color of the light. (One angstrom, 1 Å, equals 10^{-10} meters. Anders Jonas Ångström was a Swedish physicist and astronomer.)

After the introduction of the spectroscope, scientists began studying the interaction of light and matter to understand how light was emitted and absorbed by bodies of matter. Solid bodies heated to glowing emitted a continuous spectrum composed of all wavelengths of light. The intensities of the

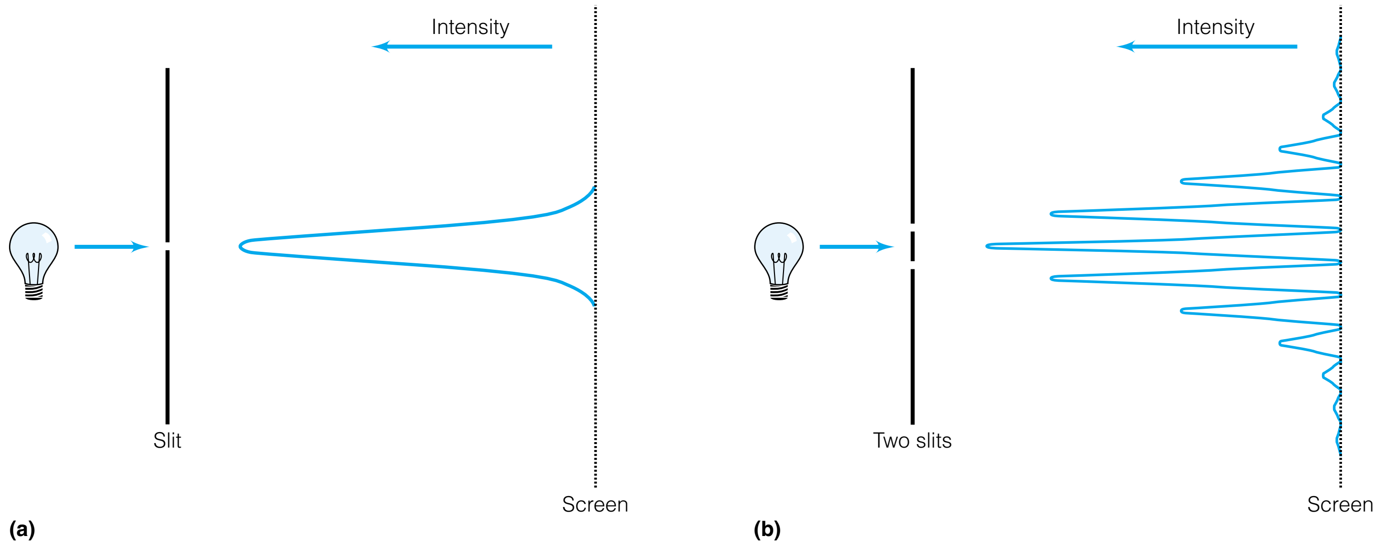

Figure 9.10 Thomas Young's "proof" that light is a wave. (a) When light is passed through a tiny slit, a single bright line is observed on a screen opposite the slit. (b) When light is passed through two closely spaced slits, a pattern of bright and dark lines is observed on the screen. This pattern is due to constructive and destructive interference of light waves.

different wavelengths of light emitted were measured and plotted. The intensity distribution presented much fuel for debate.

The easiest bodies of matter to treat theoretically were called blackbodies. A *blackbody* is a perfect absorber or emitter of radiation. The distribution of absorbed or emitted radiation depends only on the absolute temperature, not on the blackbody material. A blackbody can be approximated as a small, hollow cavity with only a tiny hole for light to escape (Figure 9.11). Light emitted by blackbodies is sometimes referred to as *cavity radiation.*

When scientists began measuring the intensity or "power density" of light given off as a function of wavelength $I(\lambda)$ at various temperatures, they made some interesting observations:

1. Not all wavelengths of light are emitted equally. At any temperature, the intensity of emitted light approaches zero as the wavelength approaches zero. It increases to some maximum intensity I_{max} at some wavelength, and then decreases back toward zero as the wavelength increased. Typical plots of the power density versus λ at specific temperatures are shown in Figure 9.12.
2. The *total* power per unit area, in units of watts per square meter (W/m^2), given off by a blackbody at any temperature is proportional to the fourth power of the absolute temperature:

$$\text{total power per unit area} = \sigma T^4 \tag{9.18}$$

where σ is the *Stefan-Boltzmann constant,* whose value is determined experimentally to be 5.6705×10^{-8} W/m$^2\cdot$K^4. This relationship was measured experimentally by the Austrian physicist Josef Stefan in 1879 and deduced by his countryman Ludwig Boltzmann several years later.
3. The wavelength at the *maximum* intensity, λ_{max}, varies indirectly with temperature such that

$$\lambda_{\text{max}} \cdot T = \text{constant} \tag{9.19}$$

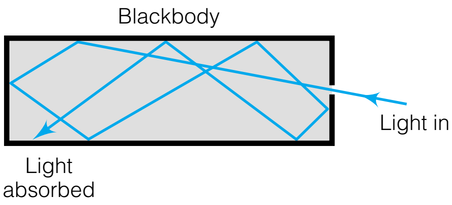

Figure 9.11 A good approximation of a blackbody is made by constructing a cavity with a very small hole in it. Defined as a perfect absorber or emitter of radiation, blackbodies do not absorb or emit radiation equally at all wavelengths. This diagram shows a blackbody's ability to absorb all radiation. Light that enters the small hole of the blackbody reflects off the inside surfaces, but has a very small chance of escaping the cavity before it is absorbed.

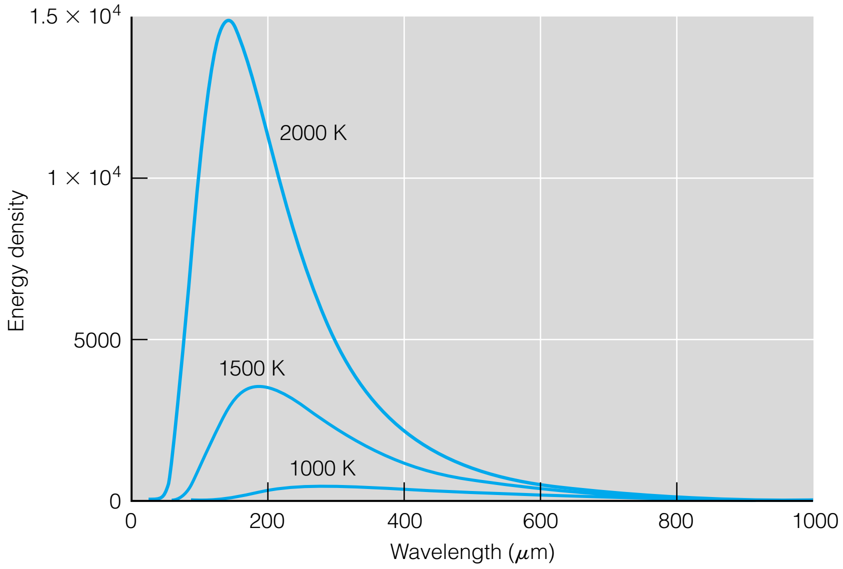

Figure 9.12 The experimentally determined behavior of blackbodies. This plot shows the intensity of light at different wavelengths for different temperatures of the blackbody. Explaining these curves theoretically was a major problem for classical mechanics.

where the value of this constant is approximately 2898 μm·K; the wavelength is in units of micrometers. This equation, enunciated by Wien in 1894, is known as the *Wien displacement law*. (This relationship is still used today to estimate the temperature of hot bodies, using an optical device called a pyrometer to determine intensities of light given off at certain wavelengths of light.)

Example 9.3

a. What is the total power per unit area emitted by a blackbody at a temperature of 1250 K?
b. If the area of the blackbody is 1.00 cm^2 (0.000100 m^2), what is the total power emitted?

Solution

a. Using equation 9.18 and the value of the Stefan-Boltzmann constant from above, one finds

$$\text{total power per unit area} = (5.6705 \times 10^{-8}\ \text{W/m}^2\cdot\text{K}^4)(1250\ \text{K})^4$$

The K^4 units cancel to yield

$$\text{total power per unit area} = 1.38 \times 10^5\ \text{W/m}^2$$

b. Since the total power per unit area is 1.38×10^5 W/m^2, for an area of 0.0001 m^2 the power emitted is

$$\text{power} = (1.38 \times 10^5\ \text{W/m}^2)(0.0001\ \text{m}^2)$$

$$\text{power} = 13.8\ \text{W} = 13.8\ \text{J/s}$$

The definition of the unit "watt" has been used for the final equality to show that 13.8 joules of energy are emitted per second.

Example 9.4

A lightbulb filament at 2500 K emits light having a maximum intensity at what wavelength?

Solution

Using the Wien displacement law, one determines

$$\lambda_{\text{max}} \cdot 2500\ \text{K} = 2898\ \mu\text{m}\cdot\text{K}$$

$$\lambda_{\text{max}} = 1.1592\ \mu\text{m or } 11{,}592\ \text{Å}$$

This wavelength of light is in the infrared region, very close to the visible light region. This does not imply that no visible light is emitted, only that the wavelength *maximum* of the emitted light lies in the infrared region of the spectrum.

There were several attempts to model blackbody radiation behavior to explain these relationships, but they were only partially successful. The most successful of these started with an assumption by the English baron Lord John W. S. Rayleigh that light waves come from tiny oscillators within the blackbody. Rayleigh assumed too that the energy of the light wave is proportional to its wavelength, so that the smaller wavelengths would be emitted more easily by these tiny oscillators. Using the equipartition principle from the kinetic theory of gases (see Chapter 19), Rayleigh proposed and later James Hopwood Jeans corrected a simple formula for the infinitesimal amount of energy per unit volume $d\rho$ (also known as an *energy density*) in a blackbody in a wavelength interval $d\lambda$ as

$$d\rho = \left(\frac{8\pi kT}{\lambda^4}\right) d\lambda \tag{9.20}$$

In this expression, k is Boltzmann's constant, λ is the wavelength, and T is the absolute temperature. The total energy per unit volume at a particular temperature is given by the integral of the above expression. Equation 9.20 is known as the *Rayleigh-Jeans law*.

Though it is an important first step in trying to model the behavior of light, the Rayleigh-Jeans law has its limitations. It fits the experimentally observed blackbody intensity curves such as those shown in Figure 9.12, but only at high temperatures and only in long-wavelength regions of the spectrum. Most problematic is the short-wavelength intensity predicted by the Rayleigh-Jeans law: it indicates that as the wavelength gets smaller, the energy density $d\rho$ given off in the wavelength interval $d\lambda$ goes up by a factor of the fourth power. (This is a consequence of the λ^4 term in the denominator of equation 9.20.) The final result is shown in Figure 9.13, which compares the Rayleigh-Jeans equation with the known blackbody behavior: the intensity predicted by the Rayleigh-Jeans law approaches infinity as the wavelength of the light approaches zero. In terms of Rayleigh's assumption, it suggests that the smaller the wavelength of the light, the less the energy of the light, and so the easier it should be for a blackbody to radiate that light. Infinite intensities, however, are impossible to obtain! It was obvious from experiments of the time that the intensity of light at shorter wavelengths does not approach infinity. Instead, the intensities tapered off to zero as the wavelength shortened. The Rayleigh-Jeans law predicts an *ultraviolet catastrophe* that does not occur.

Other attempts were made to explain the nature of light in terms of black-

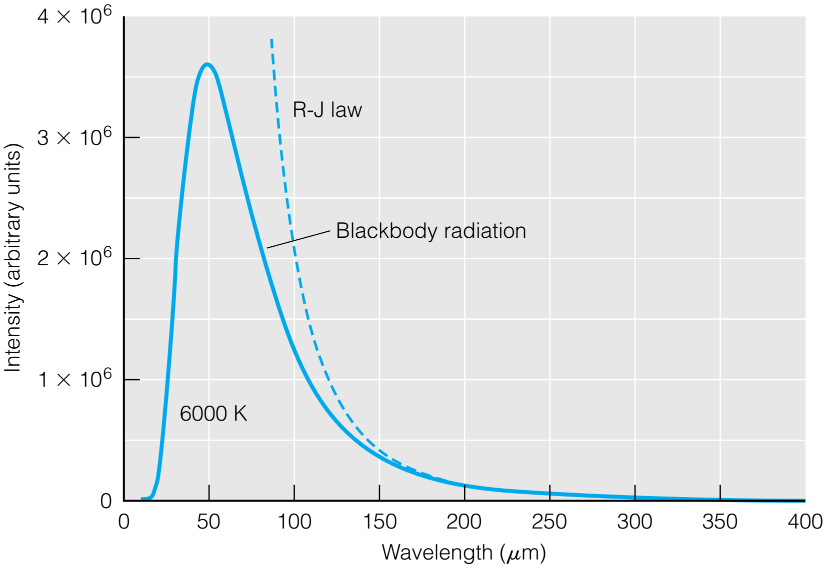

Figure 9.13 Early attempts at modeling the behavior of a blackbody included the Rayleigh-Jeans law. But as this plot illustrates, at one end of the spectrum the calculated intensity grows upward to infinity, the so-called ultraviolet catastrophe.

body radiation, but none were any more successful than the Rayleigh-Jeans law. The matter remained unsolved until 1900. All of the above unexplained phenomena remained unexplained by the accepted theories of the time. It wasn't that these theories were wrong. After hundreds of years of applying the scientific method, scientists were developing confidence that they were beginning to understand the way the universe acted. These theories were, though, incomplete. Experiments of the last 40 years of the 1800s began probing parts of the universe never before seen—the atomic universe—that could not be explained by the ideas of the time. New ideas, new theories, new ways of thinking about the universe were required.


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Figure 9.14 Max Karl Ernst Ludwig Planck (1858–1947). Planck's quantum theory, proposed in 1900, marks the beginning of modern science. Trained as a thermodynamicist, he based his theory on thermodynamic arguments. It is said that he had some misgivings about the truth of his own ideas until experimental evidence was found in support of them. The Kaiser Wilhelm Society was renamed the Max Planck Institute in his honor in 1930 and is still a major institution in Germany. He received the Nobel Prize in 1918.

9.8 Quantum Theory

The first step to a better understanding of the universe came in 1900 when the German physicist Max Karl Ernst Ludwig Planck (Figure 9.14) proposed a relatively simple equation to predict the intensities of blackbody radiation. There is some speculation that Planck came up with an equation that fit the data and then reasoned out a justification, rather than supposing a new idea and working it up to see what would happen. No matter. For our purposes, all that is important is that he was correct.

Planck was a thermodynamicist, and having studied under Kirchhoff (of spectroscope fame) in Berlin, he was aware of the blackbody problem and approached it from a thermodynamic point of view. The exact derivation is not difficult but is omitted here; texts on statistical thermodynamics include it as a matter of course. Planck treated light as interacting with electric oscillations in matter. He supposed that the energy of these oscillations was not arbitrary, but proportional to their frequency ν:

$$E = h\nu \tag{9.21}$$

where h is the proportionality constant. Planck called this amount of energy a *quantum,* and we consider that the energy of the oscillator is *quantized.* He then used statistics to derive an expression for the energy density distribution of blackbody radiation. The modern form of the equation that Planck proposed is

$$d\rho = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT} - 1}\right) d\lambda \tag{9.22}$$

where λ is the wavelength of the light, c is the speed of light, k is Boltzmann's constant, and T is the absolute temperature. The variable h represents a constant, which has units of J·s (joules times seconds) and is known as *Planck's constant.* Its value is about 6.626×10^{-34} J·s. Equation 9.22 is referred to as Planck's *radiation distribution law,* and it is the central part of Planck's *quantum theory* of blackbody radiation.

An alternate form of Planck's equation is given not in terms of the energy density but in terms of the infinitesimal *power* per unit area, or the power flux (also known as *emittance,* which is related to the intensity). Recall that power is defined as energy per unit time. In terms of the infinitesimal power per unit area $d\mathcal{E}$ emitted over some wavelength interval $d\lambda$, Planck's law is written as follows (we omit the derivation):

$$d\mathcal{E} = \frac{2\pi hc^2}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT} - 1}\right) d\lambda \tag{9.23}$$

Plots of equation 9.23 are shown in Figure 9.15. Note that they are the same as the plots of blackbody radiation, but understand that Planck's equation predicts the intensity of blackbody radiation at *all* wavelengths and *all* temperatures. Thus, by predicting the intensities of blackbody radiation, Planck's quantum theory correctly models a phenomenon that classical science could not.

Planck's equation can also be integrated from $\lambda = 0$ to ∞ in a straightforward manner to obtain

$$\mathcal{E} = \left(\frac{2\pi^5 k^4}{15c^2h^3}\right) T^4 \tag{9.24}$$

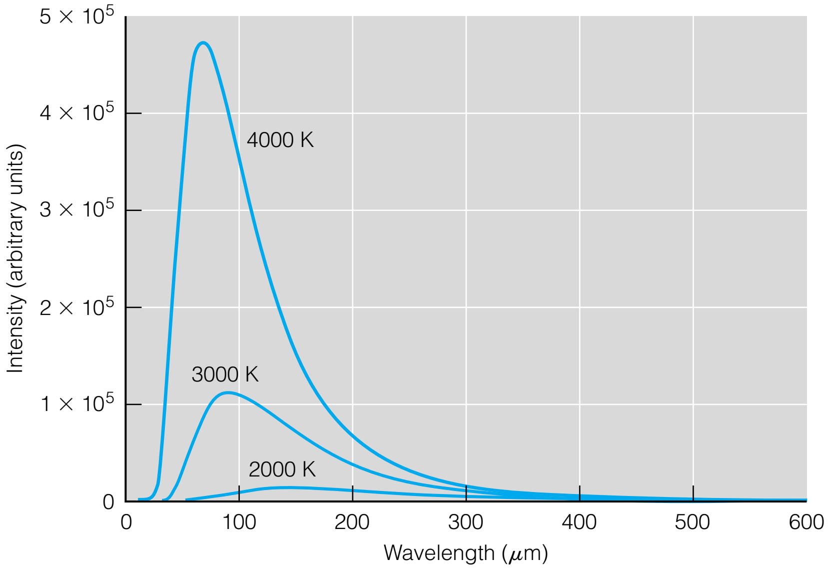


Figure 9.15 A plot of the intensity of radiation versus wavelength at different temperatures for a blackbody, assuming Planck's radiation law is correct. Predictions based on Planck's law agree with experimental measurements, suggesting a correct theoretical basis—no matter what its implications are.

where $\mathscr{E}$ is the *total power flux* (in units of $J/m^2 \cdot s$, or W/m^2) and the constants have their usual meaning. The groups of constants in parentheses illustrate that the total power flux is proportional to the fourth power of the absolute temperature. That is, Planck's equation produces the Stefan-Boltzmann law (equation 9.18) and predicts the correct value, in terms of fundamental constants, of the Stefan-Boltzmann constant σ. This was another prediction of Planck's derivation that was supported by observation.

Collectively, these correspondences suggested that Planck's derivation could not be ignored, and that the assumptions made by Planck in deriving equations 9.22 and 9.24 should not be discounted. However, many scientists (including Planck himself, initially) suspected that Planck's equations were more of a mathematical curiosity and did not have any physical importance.

Planck's quantum theory was a mere mathematical curiosity for only five years. In 1905, the 26-year-old German physicist Albert Einstein (Figure 9.16) published a paper about the photoelectric effect. In this paper, Einstein applied Planck's quantized-energy assumption not to the electrical oscillators in matter but to light itself. Thus, a quantum of light was assumed to be the energy that light has, and the amount of that energy is proportional to its frequency:

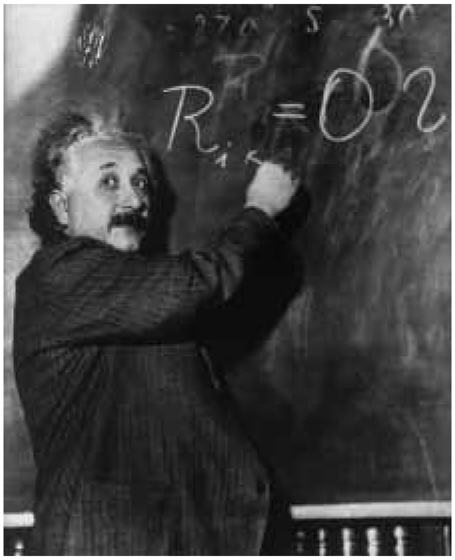


Figure 9.16 Albert Einstein (1879–1955). Einstein's work had an enormous role in the development of modern science. His 1921 Nobel Prize was awarded for his work on the photoelectric effect and the application of Planck's law to the nature of light itself. (His work on relativity was still being evaluated by experimentalists.)

$$E_{\text{light}} = h\nu$$

Einstein made several assumptions about the photoelectric effect:

1. Light is absorbed by electrons in a metal, and the energy of the light increases the energy of the electron.
2. An electron is bound to a metal sample with some characteristic energy. When light is absorbed by the electron, this binding energy must be overcome before the electron can be ejected from the metal. The characteristic binding energy is termed the *work function* of the metal and is labeled ϕ.
3. If any energy is left over energy after overcoming the work function, the excess energy will be converted to kinetic energy, or energy of motion.

Kinetic energy has the formula $\frac{1}{2}mv^2$. By assuming that each electron absorbs the energy of one quantum of light, Einstein deduced the relationship

$$h\nu = \phi + \tfrac{1}{2}mv^2 \tag{9.25}$$

where the energy of the light, $h\nu$, is converted into overcoming the work function and into kinetic energy. Needless to say, if the energy of the light is less than the work function, no electrons will be ejected because kinetic energy cannot be less than zero. The work function therefore represents a threshold energy for the photoelectric effect. Because the intensity of light is not part of the equation, changing the intensity of light does not change the speed of the ejected electrons. However, increasing the light intensity means more photons, so one would expect a greater number of electrons to be ejected. However, if the frequency of the light on the sample were increased, the kinetic energy of the ejected electrons would increase (meaning that their velocity would increase), since the work function ϕ is a constant for a particular metal. If one plotted the kinetic energy of the ejected electrons versus the frequency of light used, one should get a straight line as indicated by Figure 9.17. Using available data (Einstein was not an experimentalist!), Einstein showed that this interpretation indeed fit the facts as they were known regarding the photoelectric effect.

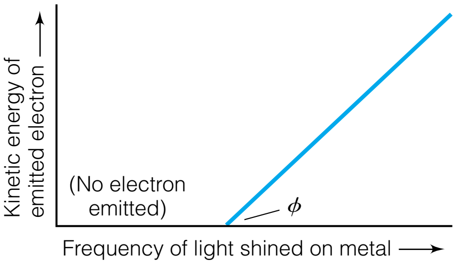


Figure 9.17 A simple diagram of the kinetic energy of an ejected electron (directly related to its speed) versus the frequency of light shined on a metal sample. Below some threshold frequency of light, no electrons are emitted. This threshold frequency, ϕ, is called the work function of the metal. The higher the frequency of light, the more kinetic energy the emitted electron has, so the faster it moves. Einstein related the frequency of the light to the kinetic energy of the ejected electrons using Planck's ideas about quantized energies, and in doing so provided an independent physical basis for Planck's radiation law as well as the concept of the quantization of light energy.

Example 9.5

a. What is the energy of one quantum of light that has a wavelength of 11,592 Å? You will need to use the relationship $c = \lambda\nu$ to convert the wavelength to a frequency. Use $c = 3.00 \times 10^8$ m/s.
b. What is the energy of one quantum of light whose frequency is given as 20,552 cm^{-1}?

Solution

a.

$$3.00 \times 10^8 \text{ m/s} = 11{,}592 \text{ Å} \cdot \left(\frac{1 \text{ m}}{10^{10}\text{Å}}\right) \cdot \nu$$

$$\nu = 2.59 \times 10^{14} \text{ s}^{-1}$$

Now, using Planck's formula from equation 9.21:

$$E = 6.626 \times 10^{-34} \text{ J·s} \times 2.59 \times 10^{14} \text{ s}^{-1}$$

$$E = 1.71 \times 10^{-19} \text{ J}$$

This is not a lot of energy. Understand, however, that this is only the energy of a single quantum of light.
b. The frequency 20,552 cm^{-1} must be converted to units of s^{-1} in order to use Planck's constant directly. With these units,

$$\text{wavenumber} = \frac{1}{\lambda}$$

so one can rearrange to get

$$\lambda = \frac{1}{\text{wavenumber}}$$

$$\lambda = \frac{1}{20.552 \text{ cm}^{-1}}$$

$$\lambda = 4.8728 \times 10^{-5} \text{ cm} = 4.8728 \times 10^{-7} \text{ m}$$

Using $c = \lambda\nu$ or $\nu = c/\lambda$:

$$\nu = \frac{3.00 \times 10^8 \text{ m/s}}{4.8728 \times 10^{-7} \text{ m}}$$

$$\nu = 6.16 \times 10^{14} \text{ s}^{-1}$$

Using Planck's constant in conjunction with this frequency:

$$E = (6.626 \times 10^{-34} \text{ J·s})(6.16 \times 10^{14} \text{ s}^{-1})$$

$$E = 4.08 \times 10^{-19} \text{ J}$$

This again is not a lot of energy.

Example 9.6

Work functions, ϕ, are usually listed in units of electron volts, eV, where 1 eV $= 1.602 \times 10^{-19}$ J. What is the velocity of an electron emitted by Li ($\phi = 2.90$ eV) if light having a frequency of $4.77 \times 10^{15} \text{ s}^{-1}$ is absorbed?

Solution

Calculating the energy of the light:

$$E = (6.626 \times 10^{-34}\ \text{J·s})(4.77 \times 10^{15}\ \text{s}^{-1})$$
$$E = 3.16 \times 10^{-18}\ \text{J}$$

Using Einstein's equation for the photoelectric effect and substituting:

$$h\nu = \phi + \tfrac{1}{2}mv^2$$
$$3.16 \times 10^{-18}\ \text{J} = (2.90\text{eV})(1.602 \times 10^{-19}\ \text{J/eV}) + \tfrac{1}{2}(9.109 \times 10^{-31}\ \text{kg}) \cdot v^2$$
$$3.16 \times 10^{-18}\ \text{J} = 4.646 \times 10^{-19}\ \text{J} + (4.555 \times 10^{-31}\ \text{kg}) \cdot v^2$$
$$v^2 = 5.92 \times 10^{12}\ \text{m}^2/\text{s}^2$$
$$v = 2.43 \times 10^{6}\ \text{m/s}$$

Verify that the units do work out to units of velocity, m/s. This velocity is about 1% of the speed of light.

This independent experimental support of Planck's radiation distribution (and Einstein's application of it to light) was not lost on the scientific community, and since 1905 this has been generally accepted as the correct understanding of light. Planck's and Einstein's work reintroduced the idea that light can be treated as a *particle*—a particle having a certain amount of energy. There was no denying the fact that light acts like a wave. It reflects, refracts, interferes as only a wave can. But there can also be no denying that light has particle properties. Light can be treated as a stream of individual particles, each of which carries a certain amount of energy whose value is determined by its wavelength.

More proof of the particle nature of light came in 1923 when Arthur Compton showed that the scattering of *monochromatic* (same-wavelength; literally, "same-color") X rays by graphite caused some of the X rays to shift to a slightly longer wavelength. The only way to account for this was to assume that the monochromatic X rays acted as a particle with a specific energy, and that the collision of a particle of light with an electron caused energy to be transferred between the two particles, lessening the energy of the light particle and therefore increasing its wavelength. (There were also momentum considerations, as we will see later.) In 1926, G. N. Lewis proposed the word *photon* as the name for a particle of light.

The value of h is approximately 6.626×10^{-34} J·s. The unit of h, joules times seconds, is necessary so that when h is multiplied by a frequency, which has units of s^{-1}, the product yields the unit of joules, which is a unit of energy. (Other values of h are used that have different units, but the idea is the same.) The numerical value of h is extremely small: on the order of 10^{-34}. The implication is that one will not even notice the packaging of energy into quanta unless one is looking at the behavior of extremely small objects, like atoms and molecules and photons. It wasn't until the late 1800s that science developed the tools (like spectroscopes) to do that, so it wasn't until then that scientists noticed the difference between discrete bundles of energy and so-called continuous energy.

Finally, the units of h, joule·second (or J·s), is a combination of energy and time. Energy multiplied by time yields a quantity known as *action*. Earlier in history, scientists developed something called the principle of least action, which is an important concept in classical mechanics. In quantum mechanics, we will find that any quantity that has units of action is intimately related to Planck's constant.

Planck's quantum theory answered one of the great unknowns of earlier science, that of blackbody radiation. There were still several unanswered questions, but quantum theory was the first breakthrough and is typically regarded as the boundary between classical and modern physics. Any development before 1900 is considered classical science; after 1900, modern. It was after 1900 that a new understanding of atoms and molecules—the basis of all chemistry—was formulated.

9.9 Bohr's Theory of the Hydrogen Atom

The next step toward an understanding of electrons in atoms was announced by Danish scientist Niels Henrik David Bohr (Figure 9.18) in 1913 in considering Rydberg's general formula, equation 9.17, for the emission lines of the hydrogen atom spectrum. However, Bohr was considering the Rydberg equation in light of two new ideas about nature: the nuclear theory of the atom, recently proposed by Rutherford, and the idea of the *quantization of a measurable quantity,* the energy of a photon. (Bohr and Einstein are generally considered the two most influential scientists of the twentieth century. Which is more influential is an ongoing debate.)

The nuclear theory of the atom assumed that the negatively charged electron was in orbit about a more massive nucleus. However, Maxwell's theory of electromagnetism requires that when charged matter changes its direction, it must emit radiation as it accelerates. But electrons in atoms don't emit radiation as they orbit the nucleus, as far as scientists could tell.

Bohr reasoned that perhaps energy was not the only quantity that could be quantized. If a particle were traveling in a circular orbit about a nucleus, *suppose its angular momentum were quantized?*

Bohr made certain assumptions, statements that were not to be justified but *assumed* as true, and from these statements he derived certain mathematical expressions about the electron in the hydrogen atom. His assumptions were:


Niels Bohr Archive, courtesy AIP Emilio Segre Visual Archives

Figure 9.18 Niels Henrik David Bohr (1885–1962). Bohr's work was vital in the development of modern science. Bohr made the leap from quantized energy to the quantization of other measurables; specifically, angular momentum of subatomic particles like electrons. Bohr and Einstein argued over many interpretations of the new theories, but Bohr won most of the arguments. Bohr almost died being smuggled out of Europe during World War II. He survived to assist in the development of the atomic bomb.

1. In the hydrogen atom, the electron moves in a circular orbit about the nucleus. Mechanically, the centripetal force that curves the path of the electron is provided by the coulombic force of attraction between the oppositely charged particles (the negatively charged electron and the positively charged proton in the nucleus).
2. The energy of the electron remains constant as the electron remains in its orbit about the nucleus. This statement was considered a violation of Maxwell's theory of electromagnetism regarding accelerating charges. Since it seems apparent that this "violation" does occur, Bohr suggested accepting that it is so.
3. Only certain orbits are allowed, each orbit having a quantized value of its angular momentum.
4. Transitions between orbits are allowed, but only when an electron absorbs or emits a photon whose energy is exactly equal to the difference between the energy of the orbits.

Assumption 1, regarding the relationship between forces, can be written as

$$F_{\text{cent}} = F_{\text{coul}} \tag{9.26}$$

where F_{cent} and F_{coul} are the centripetal force and coulombic force, respectively. Expressions for each of these quantities are known from classical mechanics, and substituting them yields

$$\frac{m_e v^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2} \tag{9.27}$$

where r is the radius of the circular orbit, e is the charge on the electron, m_e is the mass of the electron, v is the velocity of the electron, and ε_0 is a physical constant called the *permittivity of free space* (and equals 8.854×10^{-12} $\text{C}^2/\text{J}\cdot\text{m}$). The total energy of a system is simply the sum of the kinetic energy K and the potential energy V:

$$E_{\text{tot}} = K + V \tag{9.28}$$

The expressions for the kinetic energy of a moving electron, $\frac{1}{2}m_e v^2$, and the potential energy of two charged, attracting particles, $-e^2/4\pi\varepsilon_0 r$, are also known, giving

$$E_{\text{tot}} = \frac{1}{2}m_e v^2 - \frac{e^2}{4\pi\varepsilon_0 r} \tag{9.29}$$

If we rewrite Bohr's equivalence of centripetal force and coulombic force, equation 9.27, as

$$m_e v^2 = \frac{e^2}{4\pi\varepsilon_0 r} \tag{9.30}$$

we can substitute for the kinetic energy term in equation 9.29 and combine the two terms to get

$$E_{\text{tot}} = -\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 r} \tag{9.31}$$

Now Bohr's assumption 3 can be applied. Classically, if an object of mass m is traveling in a circular path with radius r about a center, the magnitude* of the angular momentum L is

$$L = mvr \tag{9.32}$$

In the SI system of units, mass has units of kg, velocity has units of m/s, and distance (the radius) has units of m. Angular momentum therefore has units of $\text{kg}\cdot\text{m}^2/\text{s}$. But also recognize that J·s can be rewritten as

$$\text{J}\cdot\text{s} = \text{N}\cdot\text{m}\cdot\text{s} = \frac{\text{kg}\cdot\text{m}}{\text{s}^2}\cdot\text{m}\cdot\text{s} = \frac{\text{kg}\cdot\text{m}^2}{\text{s}}$$

That is, Planck's constant has the same units as angular momentum! Or, restated, angular momentum has units of action. As hinted earlier, any quantity

---

*Angular momentum is a vector whose formal definition includes the cross product of the velocity vector, **v**, and the radius vector, **r**:

$$\mathbf{L} = m\mathbf{r} \times \boldsymbol{v}$$

Equation 9.32 relates the magnitude of the angular momentum only, and assumes that the velocity vector is perpendicular to the radius vector.

that has units of action can be related to h, and Bohr did just that. He assumed that the possible quantized values of the angular momentum were some multiples of h:

$$L = m_e v r = \frac{nh}{2\pi} \tag{9.33}$$

where h is Planck's constant and n is some integer $(1, 2, 3, \ldots)$ indicating that the angular momentum is some integral multiple of Planck's constant. The value of $n = 0$ is not allowed, because then the electron would have no momentum and wouldn't be orbiting the nucleus. The 2π in the denominator of equation 9.33 accounts for the fact of a complete circle having 2π radians, and Bohr assumed that the orbits of the electron were circular.

Equation 9.33 can be rewritten as

$$v = \frac{nh}{2\pi m_e r}$$

and we can substitute for velocity in equation 9.30, which is derived from Bohr's first assumption about forces. Performing this substitution and rearranging the expression to solve for the radius r, we get

$$r = \frac{\varepsilon_0 n^2 h^2}{\pi m_e e^2} \tag{9.34}$$

where all variables are as defined above. It is easy to show that this expression has units of length. Note that this equation implies that the radius of the orbit of an electron in the hydrogen atom will be a value determined by a collection of constants: ε_0, h, π, m_e, e, and the integer n. The only variable that can change is n, but it is restricted by Bohr's assumption 3 to be a positive integer. Therefore the radius of the electron orbits in the hydrogen atom can only have certain values, determined solely by n. The radius of the orbits of the electron is *quantized*. The integer denoted as n is termed a *quantum number*. A diagram of Bohr's hydrogen atom having specific radii for the electron orbits is shown in Figure 9.19.

Before leaving discussion of the radius, there are two other points to consider. Note that the expression for r depends on Planck's constant h. If Planck and others had not developed a quantum theory of light, the very concept of h would not exist, and Bohr would not have been able to rationalize his assumptions. A quantum theory of light was a necessary precursor to a quantum theory of matter—or at least, a theory of hydrogen. Second, the smallest value of r corresponds to a value of 1 for the quantum number n. Substituting values for all of the other constants, whose values were known in Bohr's time, one finds that for $n = 1$:

$$r = 5.29 \times 10^{-11} \text{ m} = 0.529 \text{ Å}$$

This distance ends up being an important yardstick for atomic distances and is called the *first Bohr radius*. This meant, by the way, that the hydrogen atom was about 1 Å in diameter. At that time, science (including theoretical work by Einstein on Brownian motion) was just beginning to estimate the size of atoms. This predicted radius fell exactly where it should be from experimental considerations.

The total energy of a system is of paramount interest, and by using the expression for the quantized radius for the electron in a hydrogen atom, one can

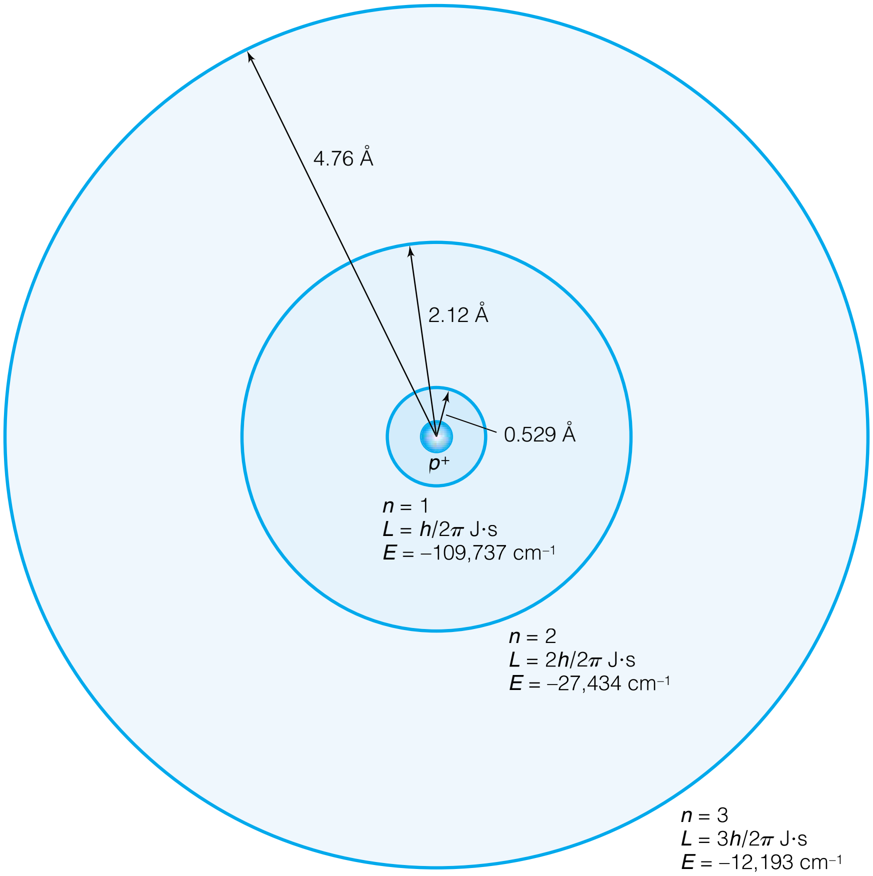


Figure 9.19 The Bohr model of the hydrogen atom—shown here with its three lowest-energy states—is not a correct description, but it was a crucial step in the development of modern quantum mechanics.

substitute for the radius in the expression for the total energy, equation 9.31, to obtain

$$E_{\text{tot}} = -\frac{m_e e^4}{8\varepsilon_0^2 n^2 h^2} \tag{9.35}$$

or the total energy of the hydrogen atom. It is simple to demonstrate that this expression has units of energy:

$$\frac{\text{kg}\cdot\text{C}^4}{(\text{C}^2/\text{J}\cdot\text{m})^2(\text{J}\cdot\text{s})^2} = \frac{\text{kg}\cdot\text{C}^4\ \text{J}^2\text{m}^2}{\text{C}^4\text{J}^2\text{s}^2}$$

$$= \frac{\text{kg}\cdot\text{m}^2}{\text{s}^2} = \text{J}$$

Again, note that the total energy, like the radius, is dependent on a collection of constants and a number, n, that is restricted to integer values. *The total energy of the hydrogen atom is quantized.*

Finally, Bohr's assumption 4 dealt with changes in energy levels. The difference between a final energy, E_f, and an initial energy, E_i, is defined as ΔE:

$$\Delta E = E_f - E_i \tag{9.36}$$

Bohr stated that this ΔE must equal the energy of the photon:

$$\Delta E = h\nu \tag{9.37}$$

Now that Bohr had derived an equation for the total energies of the hydrogen atom, he could substitute into equations 9.36 and 9.37:

$$\begin{aligned} \Delta E = h\nu = E_\mathrm{f} - E_\mathrm{i} &= \left(-\frac{m_\mathrm{e}e^4}{8\varepsilon_0^2 n_\mathrm{f}^2 h^2} + \frac{m_\mathrm{e}e^4}{8\varepsilon_0^2 n_\mathrm{i}^2 h^2}\right) \\ &= \frac{m_\mathrm{e}e_4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_\mathrm{i}^2} - \frac{1}{n_\mathrm{f}^2}\right) \end{aligned} \tag{9.38}$$

For emission, ΔE is negative (that is, energy is given off), and for absorption ΔE is positive (energy is absorbed). In terms of wavenumber $\tilde{\nu}$, equation 9.38 becomes

$$\tilde{\nu} = \frac{m_\mathrm{e}e^4}{8\varepsilon_0^2 h^3 c}\left(\frac{1}{n_\mathrm{i}^2} - \frac{1}{n_\mathrm{f}^2}\right) \tag{9.39}$$

Compare this with Rydberg's equation, 9.17. It is the same expression! Bohr therefore derived an equation that predicts the spectrum of the hydrogen atom. Also, Bohr is predicting that the Rydberg constant R_H is

$$R_\mathrm{H} = \frac{m_\mathrm{e}e^4}{8\varepsilon_0^2 h^3 c} \tag{9.40}$$

Substituting for the values of the constants as they were known at that time, Bohr calculated from his assumptions a value for R_H that differed less than 7% from the experimentally determined value. Current accepted values for the constants in equation 9.40 yield a theoretical value for R_H that differs by less than 0.1% from the experimental value. (This can be made even closer to experimental values by using the reduced mass of the H atom, rather than the mass of the electron. We will consider reduced masses in the next chapter.)

The importance of this conclusion cannot be overemphasized. By using some simple classical mechanics, ignoring the problem with Maxwell's electromagnetic theory, and making one single new assumption—the quantization of angular momentum of the electron—Bohr was able to deduce the spectrum of the hydrogen atom, a feat unattained by classical mechanics. By deducing the value of the Rydberg constant, an experimentally determined parameter, Bohr was showing the scientific community that new ideas about nature were crucial to the understanding of atoms and molecules. Scientists of his time were unable to shrug off the fact that Bohr had come up with a way to understand the spectrum of an atom, whatever the source of the derivation. This crucial step, regarding other measurable quantities like angular momentum as quantized, was what made the Bohr theory of the hydrogen atom one of the most important steps in the modern understanding of atoms and molecules.

The limitations of Bohr's conclusion, however, also cannot be forgotten. It applies to the hydrogen atom, and *only* the hydrogen atom. Therefore it is limited, and it is not applicable to any other element that has more than one electron. The Bohr theory is, however, applicable to an atomic system that has only a single electron (which means that the systems involved were highly charged cations), and the ultimate equation for the energy of the system is revised to

$$E_\mathrm{tot} = -\frac{Z^2 m_\mathrm{e}e^4}{8\varepsilon_0^2 n^2 h^2} \tag{9.41}$$

where Z is the charge on the nucleus. So Bohr's theory is applicable to U^{91+}, which has all but one of its electrons stripped from its nucleus. (However, relativistic effects will be present, so applicability of Bohr's equation is even more limited.) Unfortunately, most matter of interest to chemists is not composed of single-electron atoms, and the Bohr theory is inherently limited.

But it opened the eyes of contemporary scientists to new ideas: ideas that some measurable quantities, called *observables,* are not continuous in their possible values, like positions in a number line. Rather, they are discrete or *quantized,* and can have only certain values. This idea became one of the central tenets of the new quantum mechanics.

9.10 The de Broglie Equation

Between the introduction of Bohr's theory and the development of quantum mechanics, there was very little in the way of new contributions to the understanding of matter—except for an important idea put forth by Louis de Broglie in 1924. De Broglie, a scientist whose family was part of the French aristocracy, hypothesized that if a wave like light can have particle properties, why can't particles like electrons, protons, and so on have *wave* properties?

We can understand de Broglie's hypothesis by equating the expression for energy from special relativity and from quantum theory:

$$E = mc^2$$

$$E = h\nu$$

Therefore

$$mc^2 = h\nu$$

Since $c = \lambda\nu$ (that is, the speed of light equals its frequency times its wavelength; this is a standard conversion), we can substitute for the frequency ν:

$$mc^2 = \frac{hc}{\lambda}$$

Canceling c out of both sides and realizing that c is a velocity and that mass times velocity is momentum p, we can rearrange:

$$\lambda = \frac{h}{mc} = \frac{h}{p}$$

De Broglie suggested that this relationship applied to particles, for which the momentum equals mass times velocity ($p = mv$). The *de Broglie equation* is written for particles as

$$\lambda = \frac{h}{mv} = \frac{h}{p} \tag{9.42}$$

This equation states that the wavelength of a particle is inversely proportional to its momentum, mv, and the proportionality constant is h, Planck's constant. That is, de Broglie's equation implies that a particle of mass m acts as a wave. Only a wave, remember, can have a wavelength.

That photons have momentum was hinted at experimentally only one year before when Compton announced the change of energy of X rays upon deflection by graphite. This Compton effect involves a simultaneous transfer of energy and momentum when a photon collides with an electron. An understanding of the conservation of energy as well as the conservation of momentum allowed one to correctly predict not only the new energies of the photons but also their new directions of motion. If waves have particle properties, perhaps it is not too far-fetched to consider that matter can have wave properties.

Consider two examples that illustrate the importance of the de Broglie equation. First, if a baseball having a mass of 150 grams (which is 0.150 kg) were traveling at a speed of 150 kilometers per hour (which is 41.6 meters per second), its de Broglie wavelength would be

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{J}\cdot\text{s}}{(0.150\ \text{kg})(41.6\ \text{m/s})} = 1.06 \times 10^{-34}\ \text{m}$$

A wavelength of a millionth of a billionth of a billionth of an angstrom is undetectable even under modern conditions. The wavelength of the baseball would never be noticed, not by scientists of the late nineteenth century (or even a baseball player).

The second example is an electron, which is much smaller than a baseball. Since the de Broglie wavelength is inversely proportional to mass, we would expect that the de Broglie wavelength of a particle gets larger as the particle gets smaller. For an electron moving at the same speed as the baseball, its de Broglie wavelength is

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{J}\cdot\text{s}}{(9.109 \times 10^{-31}\ \text{kg})(41.6\ \text{m/s})} = 1.75 \times 10^{-5}\ \text{m}$$

which is 17.5 microns. This “wavelength” corresponds to the infrared region of light! Even in the late nineteenth century, this wavelength could have been detected.

Electrons typically move at higher speeds than this, and their de Broglie wavelengths are typically shorter, in the range equivalent to X rays. Since X rays were known by then to be diffracted by crystals, why not diffract electrons? In 1925, Clinton Joseph Davisson did just that. After accidentally breaking a vacuum tube with a nickel sample in it, Davisson reconditioned the nickel sample by heating it and formed large nickel crystals. Aware of de Broglie’s ideas, Davisson (with coworker Lester H. Germer) exposed a nickel crystal to electrons and found a diffraction pattern exactly as one would expect if electrons were indeed waves. This diffraction of particles showed that the particles did have wave properties, as predicted by de Broglie. Additional work confirming the wave nature of electrons was performed later that year by G. P. Thomson, the son of J. J. Thomson, who in 1897 had discovered the electron as a *particle*. The wave-particle dual nature of particles (as well as photons) has been a cornerstone of modern science ever since.

Example 9.7

Calculate the de Broglie wavelength of a 1000-kg automobile traveling at 100 kilometers per hour and of an electron traveling at 1% of the speed of light ($0.01c = 3.00 \times 10^{6}$ m/s).

Solution

For the automobile:

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{J}\cdot\text{s}}{(1000\ \text{kg})(100\ \text{km/hr})(1\ \text{hr/3600 s})(1000\ \text{m/km})}$$

$$\lambda = 2.39 \times 10^{-38}\ \text{m}$$

For the electron:

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{J}\cdot\text{s}}{(9.109 \times 10^{-31}\ \text{kg})(3.00 \times 10^{6}\ \text{m/s})}$$

$$\lambda = 2.43 \times 10^{-10}\ \text{m} \qquad \text{or} \qquad 2.43\ \text{Å}$$

The de Broglie wavelength of the automobile is unnoticeable even using modern methods. The de Broglie wavelength of the electron is similar to that of X rays, which are certainly noticeable under the right conditions.

De Broglie's insight and the Davisson-Germer experiment ultimately pointed out that matter has wave properties. For large pieces of matter, the wave properties can be ignored, but for small pieces of matter like electrons, they cannot. Because classical mechanics did not consider matter as *waves,* it was inadequate to describe the behavior of matter.

9.11 Summary: The End of Classical Mechanics

By 1925 it was realized that the classical ideas that described matter didn't work at the atomic level. Some progress—Planck's quantum theory, Einstein's application of quantum theory to light, Bohr's theory of hydrogen, de Broglie's relationship—had been made, but it was all very specific and not generally applied to atoms and molecules.

It took a generation for new thinkers, exposed to the new and fantastic ideas of the last quarter century, to propose the new theories. It has been debated philosophically whether new thinkers were required; would older scientists still be bound by the old theories and be unable to come up with totally new ideas?

In 1925–1926, the German physicist Werner Heisenberg and the Austrian physicist Erwin Schrödinger independently and from different perspectives published initial works announcing the formation of *quantum mechanics,* a new way of thinking of electrons and their behavior. From their basic arguments, an entirely new concept of atoms and molecules was constructed. Most importantly, this picture of atoms and molecules survives because it answers the questions about atomic and molecular structure, and it does so in a more complete way than any theory before or since. As with most theories, quantum mechanics is based on a set of assumptions called *postulates.* Some of these postulates seem, and certainly seemed to fellow scientists in 1925, a totally new way of thinking about nature. But as one concedes the success of quantum mechanics, it becomes easier to accept the postulates as factual and then try to come to grips with what they mean.

Before we consider quantum mechanics itself, it is important to understand that we will be applying quantum mechanics to atomic and molecular behavior, not to the behavior of large macroscopic objects. Ordinary, classical mechanics can be used to understand the behavior of a baseball, but not an electron. It is completely analogous to using Newton's equations to understand the velocity of a car going 100 km/hr, but using Einstein's equations of relativity to understand the velocity of a car at near the speed of light. Although one could use relativity equations to model very slow speeds, it is impractical within the limits of measurement. So it is with quantum mechanics. It applies to all matter, but it is not needed to describe the behavior of something the size of a baseball. By the end of the nineteenth century, scientists began probing matter the size of atoms for the first time, and their observations couldn't be explained using classical mechanics. That's because they were assuming that atoms behaved in the manner described by Newton, and they don't. Individual electrons and atoms require a different model to explain their behavior.

Most basic quantum mechanics was developed by 1930. However, the development of quantum mechanics as applied to electrons also led to new theories of the nucleus, all of which today inherently contain quantum assumptions. Today, quantum mechanics encompasses the entire behavior of the atom. Because chemistry starts with atoms, quantum mechanics provides the very basis of modern chemical science.

EXERCISES FOR CHAPTER 9

9.2 Laws of Motion

9.1. For an object having mass m falling in the z direction, the kinetic energy is $\frac{1}{2}m\dot{z}^2$ and the potential energy is mgz, where g is the gravitational acceleration constant (approximately 9.8 m/s^2) and z is the position. For this one-dimensional motion, determine the Lagrangian function L and write the Lagrangian equation of motion.

9.2. For the system in Exercise 9.1, determine the Hamiltonian equation of motion.

9.3. For Exercise 9.2, verify that equations 9.14 and 9.15 are valid for the Hamiltonian you derived.

9.4. **(a)** A block of wood being pushed up an inclined plane has certain forces acting on it: the force of pushing, the force of friction, the force due to gravity. Whose equations of motion are best suited to describing this system, and why? **(b)** Answer the same question but now for a rocket whose velocity and altitude above ground are constantly being monitored.

9.3–9.7 Unexplainable Phenomena

9.5. Draw, label, and explain the functions of the parts of a spectroscope.

9.6. Convert **(a)** a wavelength of 218 Å to cm^{-1}, **(b)** a frequency of 8.077×10^{13} s^{-1} to cm^{-1}, **(c)** a wavelength of 3.31 μm to cm^{-1}.

9.7. What conclusion can be drawn from the fact that two spectra of two different compounds have certain lines at exactly the same wavelengths?

9.8. Explain why no lines in the Balmer series of the hydrogen atom spectrum have wavenumbers larger than about 27,434 cm^{-}1. (This is called the *series limit*.)

9.9. What are the series limits (see the previous problem) for the Lyman series ($n_2 = 1$) and the Brackett series ($n_2 = 4$)?

9.10. The following are the numbers n_2 for some of the series of lines in the hydrogen atom spectrum:

Lyman: 1 Balmer: 2 Paschen: 3 Brackett: 4 Pfund: 5

Calculate the energy changes, in cm^{-1}, of the lines in each of the stated series for each of the given values for n_1: **(a)** Lyman, $n_1 = 5$; **(b)** Balmer, $n_1 = 8$; **(c)** Paschen, $n_1 = 4$; **(d)** Brackett, $n_1 = 8$; **(e)** Pfund, $n_1 = 6$.

9.11. Given that the wavelengths of the first three lines of the Balmer series are 656.2, 486.1, and 434.0 nm, calculate an average value of R.

9.12. From the numbers determined by Millikan, what was the value of the charge-to-mass ratio, e/m, in units of C/kg?

9.13. **(a)** Using the identities of alpha (a helium nucleus) and beta (an electron) particles as well as the masses of the proton, neutron, and electron, estimate how many beta particles it takes to make up the mass of one alpha particle. **(b)** From this result, would you expect an alpha particle or a beta particle of the same kinetic energy to be the faster-moving radioactive emission? **(c)** Does your answer to part b justify the experimental observation that beta particles are more penetrating than alpha particles?

9.14. **(a)** How much radiant energy is given off, in watt/meter^2, by an electric stove heating element that has a temperature of 1000 K? **(b)** If the area of the heating element is 250 cm^2, how much power, in watts, is being emitted?

9.15. Stefan's law, equation 9.18, suggests that any body of matter, no matter what the temperature, is emitting energy. At what temperature would a piece of matter have to be in order to radiate energy at the flux of 1.00 W/m^2? At the flux of 10.00 W/m^2? 100.00 W/m^2?

9.16. An average human body has a surface area of 0.65 m^2. At a body temperature of 37°C, how many watts (or J/s) of power does a person emit? (Understanding such emissions is important to NASA and other space agencies when designing space suits.)

9.17. The surface temperature of our sun is about 5800 K. Assuming that it acts as a blackbody: **(a)** What is the power flux radiated by the sun, in W/m^2? **(b)** If the surface area of the sun is 6.087×10^{12} m^2, what is the total power emitted in watts? **(c)** Since watts are J/s, how many joules of energy are radiated in one year (365 days)? (Note: The sun is actually a very poor approximation of a blackbody.)

9.18. The slope of the plot of energy versus wavelength for the Rayleigh-Jeans law is given by a rearrangement of equation 9.20:

$$\frac{d\rho}{d\lambda} = \frac{8\pi kT}{\lambda^4}$$

What are the value and units of this slope for a blackbody having the following temperatures and at the following wavelengths? **(a)** 1000 K, 500 nm; **(b)** 2000 K, 500 nm; **(c)** 2000 K, 5000 nm; **(d)** 2000 K, 10,000 nm. Do the answers indicate the presence of an ultraviolet catastrophe?

9.19. **(a)** Use Wien's law to determine the λ_{max} of the sun if its surface temperature is 5800 K. **(b)** The human eye sees light most efficiently if the light has a wavelength of 5000 Å (1 Å = 10^{-10} m), which is in the green-blue portion of the spectrum. To what blackbody temperature does that correspond? **(c)** Compare your answers from the first two parts and comment.

9.8 Quantum Theory

9.20. The slope of the plot of energy versus wavelength for Planck's law is given by a rearrangement of equation 9.22:

$$\frac{d\rho}{d\lambda} = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT} - 1}\right)$$

Give the value and units of this slope for a blackbody having the following temperatures and at the following wavelengths: **(a)** 1000 K, 500 nm; **(b)** 2000 K, 500 nm; **(c)** 2000 K, 5000 nm; **(d)** 2000 K, 10,000 nm; **(e)** Compare these results to those for problem 9.18. **(f)** At what temperatures and spectral regions will the Rayleigh-Jeans law be close to Planck's law?

9.21. Integrate Planck's law (equation 9.23) from the wavelength limits $\lambda = 0$ to $\lambda = \infty$ to get equation 9.24. You will have to rewrite the expression by redefining the variable (and its infinitesimal) and use the following integral:

$$\int_0^\infty \frac{x^3}{e^x - 1}\,dx = \frac{\pi^4}{15} \qquad \textbf{(9.43)}$$

9.22. Calculate the power of light in the wavelength range $\lambda = 350\text{–}351$ nm (that is, let $d\lambda$ be $\Delta\lambda = 1$ nm in Planck's law, and let λ be 350.5 nm) at temperatures of 1000 K, 3000 K, and 10,000 K.

9.23. Verify that the collection of constants in equation 9.24 reproduces the correct (or close to it) value of the Stefan-Boltzmann constant.

9.24. Work functions ϕ are typically given in units of electron volts, or eV. 1 eV equals 1.602×10^{-19} J. Determine the minimum wavelength of light necessary to overcome the work function of the following metals ("minimum" implies that the excess kinetic energy, $\frac{1}{2}mv^2$, is zero): Li, 2.90 eV; Cs, 2.14 eV; Ge, 5.00 eV.

9.25. Determine the speed of an electron being emitted by rubidium ($\phi = 2.16$ eV) when light of the following wavelengths is shined on the metal in vacuum: **(a)** 550 nm, **(b)** 450 nm, **(c)** 350 nm.

9.26. The photoelectric effect is used today to make light-sensitive detectors; when light hits a sample of metal in a sealed compartment, a current of electrons may flow if the light has the proper wavelength. Cesium is a desirable component for such detectors. Why?

9.27. Calculate the energy of a single photon in joules and the energy of a mole of photons in J/mol for light having wavelengths of 10 m (radio and TV waves), 10.0 cm (microwaves), 10 microns (infrared range), 550 nm (green light), 300 nm (ultraviolet), and 1.00 Å (X rays). Do these numbers explain the relative danger of electromagnetic radiation of differing wavelengths?

9.9 Bohr's Theory of Hydrogen

9.28. Show that both sides of equation 9.27 reduce to units of force, or N.

9.29. Use equation 9.34 to determine the radii, in meters and angstroms, of the fourth, fifth, and sixth energy levels of the Bohr hydrogen atom.

9.30. Calculate the energies of an electron in the fourth, fifth, and sixth energy levels of the Bohr hydrogen atom.

9.31. Calculate the angular momenta of an electron in the fourth, fifth, and sixth energy levels of the Bohr hydrogen atom.

9.32. Show that the collection of constants given in equation 9.40 gives the correct numerical value of the Rydberg constant.

9.33. Equations 9.33 and 9.34 can be combined and rearranged to find the quantized velocity of an electron in the Bohr hydrogen atom. **(a)** Determine the expression for the velocity of an electron. **(b)** From your expression, calculate the velocity of an electron in the lowest quantized state. How does it compare to the speed of light? ($c = 2.9979 \times 10^8$ m/s) **(c)** Calculate the angular momentum $L = mvr$ of the electron in the lowest energy state of the Bohr hydrogen atom. How does this compare with the assumed value of the angular momentum from equation 9.33?

9.34. **(a)** Compare equations 9.31, 9.34, and 9.41 and propose a formula for the radius of a hydrogen-like atom that has atomic charge Z. **(b)** What is the radius of a U^{91+} ion if the electron has a quantum number of 100? Ignore any possible relativistic effects.

9.10 The de Broglie Equation

9.35. The de Broglie equation for a particle can be applied to an electron orbiting a nucleus if one assumes that the electron must have an exact integral number of wavelengths as it covers the circumference of the orbit having radius r: $n\lambda = 2\pi r$. From this, derive Bohr's quantized angular momentum postulate.

9.36. What is the wavelength of a baseball having mass 100.0 g traveling at a speed of 160 km/hr? What is the wavelength of an electron traveling at the same speed?

9.37. What velocity must an electron have in order to have a de Broglie wavelength of 1.00 Å? What velocity must a proton have in order to have the same de Broglie wavelength?

Symbolic Math Exercises

9.38. Plot Planck's law of energy density versus wavelength at various temperatures. Integrate it to show that you can get the Stefan-Boltzmann law and constant.

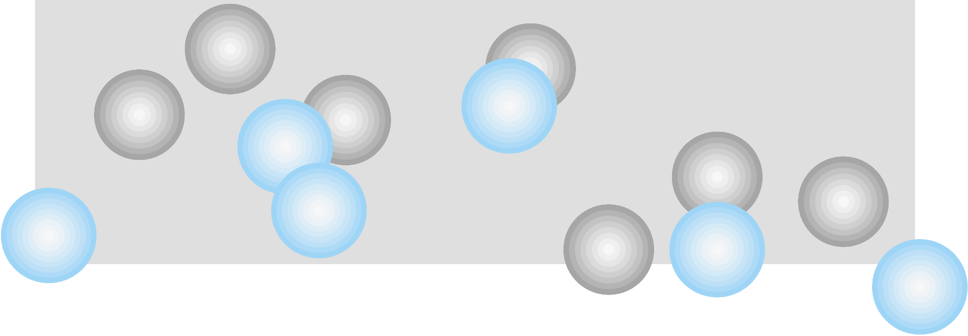
9.39. Determine under what conditions of temperature and wavelength the Rayleigh-Jeans law approximates Planck's law.

9.40. Using the second-order differential equation for the motion of a harmonic oscillator, find solutions to the equation and plot them versus time.

9.41. Construct a table of the first 50 lines of the first six series of the hydrogen atom spectrum. Can you predict the series limit in each case?

10

Introduction to Quantum Mechanics



NEW DISCOVERIES PROMPTED THE NEED for a better theory to describe the behavior of matter at the atomic level, as indicated in the previous chapter. This better theory, called *quantum mechanics,* represented a completely new way of modeling nature. Quantum mechanics ultimately showed that it provides a better basis for describing, explaining, and predicting behavior at the atomic and molecular level. As with any theory in science, quantum mechanics is accepted by scientists because it *works.* (It is, quite frankly, one of the most successfully tested theories devised by science.) That is, it provides a theoretical background that makes predictions that agree with experiment. There may be certain conceptual difficulties at first. A common question from a student is "Why is quantum mechanics this way?" The philosophy of quantum mechanics is left to the philosopher. Here, we want to see how quantum mechanics is defined and how to apply it to atomic and molecular systems.

Quantum mechanics is based on several statements called *postulates.* These postulates are assumed, not proven. It may seem difficult to understand why an entire model of electrons, atoms, and molecules is based on assumptions, but the reason is simply because the statements based on these assumptions lead to predictions about atoms and molecules that agree with our observations. Not just a few isolated observations: over decades, millions of measurements on atoms and molecules have yielded data that agree with the conclusions based on the few postulates of quantum mechanics. With agreement between theory and experiment so abundant, the unproven postulates are accepted and no longer questioned. In the following discussion of the fundamentals of quantum mechanics, some of the statements may seem unusual or even contrary. However questionable they may seem at first, realize that statements and equations based on these postulates agree with experiment and so constitute an appropriate model for the description of subatomic matter, especially electrons.

10.1 Synopsis

Quantum mechanics is sometimes difficult at first glance, partly because some new ideas and some new ways of thinking about matter are involved. These ideas will be discussed in detail in the sections that follow. Briefly, however, it might be useful to summarize these ideas so that the reader will understand where the material is headed. Remember that the ultimate goal is to have a theory that proposes how matter behaves, and that predicts events that agree with observation; that is, to have theory and experiment agree. Otherwise, a different theory is necessary to understand the experiment.

The main ideas are:

- The behavior of electrons, by now known to have wavelike properties, can be described by a mathematical expression called a wavefunction.
- The wavefunction contains within it all possible information that can be known about a system.
- Wavefunctions are not arbitrary mathematical functions, but must satisfy certain simple conditions. For example, they must be continuous.
- The most important condition is that the wavefunction must satisfy the time-dependent Schrödinger equation. With certain assumptions, time can be separated from the wavefunction, and what remains is a time-*independent* Schrödinger equation. We focus mainly on the time-independent Schrödinger equation in this text.
- In the application of these conditions to real systems, wavefunctions are found that do indeed yield information that agrees with experimental observations of these systems: *quantum mechanics predicts values that agree with experimentally determined measurements.* The simplest real system to understand, covered in the next chapter, is the hydrogen atom, a system that Rydberg and Balmer and Bohr had studied with different degrees of success. To the extent that quantum mechanics not only reproduces their success but also extends it, quantum mechanics is superior to their theories trying to describe the behavior of subatomic particles.

The rest of this chapter expands on the above ideas. A proper understanding of quantum mechanics requires an understanding of the principles that it uses. An adequate familiarity with these principles is essential, even irreplaceable. In your dealings with these principles, do not lose sight of that last statement in the above synopsis: quantum mechanics properly describes the behavior of matter, as determined by observation.

10.2 The Wavefunction

The behavior of a wave can be expressed as a simple mathematical function. For example,

$$y = A \sin (Bx + C) + D \tag{10.1}$$

is a general expression for the amplitude, y, of a sine-type (or sinusoidal) wave traveling in the x dimension. The constants A, B, C, and D have certain values that specify exactly what the sine wave looks like.

Since de Broglie indicated that matter should have wave properties, why not describe the behavior of matter using an expression for a wave? The first postulate of quantum mechanics is that the state of a system can be described by an expression called a *wavefunction.* Wavefunctions in quantum mechanics are typically given the symbol ψ or Ψ (the Greek letter psi). For various physical and mathematical reasons, these Ψ's are limited, or *constrained,* to being functions that are:

1. Single-valued (that is, a wavefunction must have only one possible $F(x)$ value for each and every value of x.)
2. Continuous
3. Differentiable (that is, there must be no mathematical reasons why the derivative of Ψ cannot exist.)*

Among other things, this last restriction prohibits functions that approach either positive or negative infinity, except maybe for individual points in the function. Another way to state this is that the function is *bounded*. For whatever variable(s) exist in the wavefunctions, these limitations must be satisfied for the entire variable range. In some cases, the range of the variable may be $+\infty$ to $-\infty$. In other cases, the variables may be limited to a certain range. Functions that meet all these criteria are considered acceptable wavefunctions. Those that do not may not provide any physically meaningful conclusions. Figure 10.1 shows some examples of acceptable and unacceptable wavefunctions.

The final part of this first postulate is that all possible information about the various observable properties of a system must be derived from the wavefunction. This seems an unusual statement at first. Later in the chapter we can fully develop this idea. But the point should be made immediately upon introduction of the wavefunction: All information must be determined solely from the function that is now defined as the wavefunction of the particle. This fact gives the wavefunction a central role in quantum mechanics.

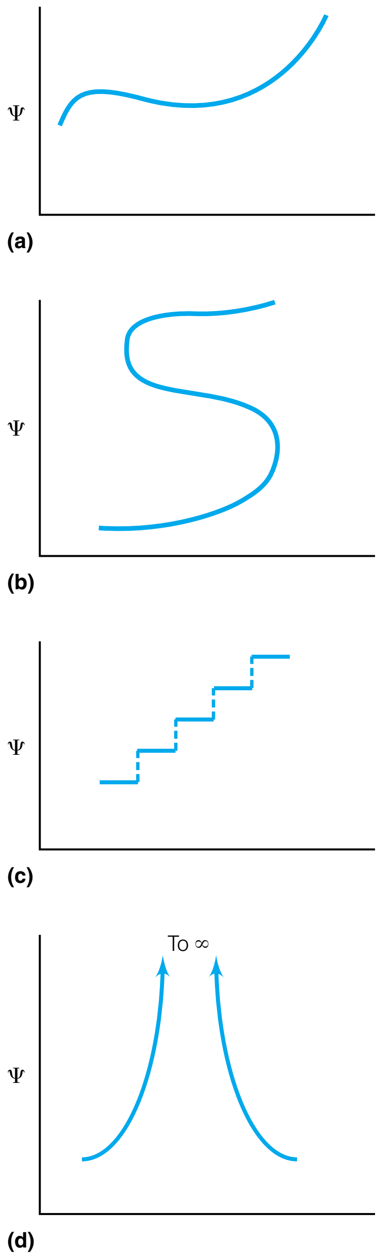


Figure 10.1 (a) An acceptable wavefunction is continuous, single-valued, bounded, and integrable. (b) This function is not single-valued and is not an acceptable wavefunction. (c) This function is not continuous and is not an acceptable wavefunction. (d) This function is not bounded and is not an acceptable wavefunction.

Example 10.1

Which of the following expressions are acceptable wavefunctions, and which are not? For those that are not, state why.

a. $f(x) = x^2 + 1$, where x can have any value

b. $f(x) = \pm\sqrt{x}$, $x \geq 0$

c. $\Psi = \dfrac{1}{\sqrt{2}} \sin \dfrac{x}{2}$, $-\dfrac{\pi}{2} \leq x \leq \dfrac{\pi}{2}$

d. $\Psi = \dfrac{1}{4 - x}$, $0 \leq x \leq 10$

e. $\Psi = \dfrac{1}{4 - x}$, $0 \leq x \leq 3$

Solution

a. Not acceptable, because as x approaches positive or negative infinity, the function also approaches infinity. It is not bounded.

b. Not acceptable, because the function is not single-valued.

c. Acceptable, because it meets all criteria for acceptable wavefunctions.

d. Not acceptable, because the function approaches infinity for $x = 4$, which is part of the range.

e. Acceptable, because the function meets all criteria for acceptable wavefunctions within that stated range of the variable x. (Compare this to the conclusion reached in part d.)

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*Many Ψ's must also be square-integrable; that is, the integral of $|\Psi|^2$ must also exist. However, this is not an absolute requirement.

10.3 Observables and Operators

When studying the state of a system, one typically makes various measurements of its properties, such as mass, volume, position, momentum, and energy. Each individual property is called an *observable.* Since quantum mechanics postulates that the state of a system is given by a wavefunction, how does one determine the value of various observables (say, position or momentum or energy) from a wavefunction?

The next postulate of quantum mechanics states that in order to determine the value of an observable, you have to perform some mathematical operation on a wavefunction. This operation is represented by an *operator.* An operator is a mathematical instruction: "Do something to this function or these numbers." In other words, an operator acts on a function (or functions) to produce a function. (Constants are special types of functions, ones that do not change value.)

For example, in the equation $2 \times 3 = 6$, the operation is multiplication and the operator is $\times$. It implies, "Multiply the two numbers together." In fancier terms, we can define the multiplication operation with some symbol, designated $\widehat{M}(a, b)$. Its definition can be "Take two numbers and multiply them together." Therefore,

$$\widehat{M}(2, 3) = 6$$

is our fancy way of writing multiplication. $\widehat{M}$ is our *multiplication operator,* where the ^ signifies an operator.

Operators can operate on functions as well as numbers. Consider the differentiation of a simple function, $F(x) = 3x^3 + 4x^2 + 5$, with respect to x:

$$\frac{d}{dx}(3x^3 + 4x^2 + 5) = 9x^2 + 8x$$

This could also be represented using simply $F(x)$ to represent the function:

$$\frac{d}{dx}F(x) = 9x^2 + 8x$$

The operator is d/dx, and can be represented by some symbol, say $\widehat{D}$, so that the above expression can be simplified to

$$\widehat{D}[F(x)] = 9x^2 + 8x$$

The operator operated on a function and generated another function. It is common to use a symbol to represent an operator, because some operators can have relatively complex forms. In applying a more complicated mathematical operation, say $(-h^2/8\pi^2 m)(d^2/dx^2)$, to a wavefunction Ψ, we could write

$$\frac{-h^2}{8\pi^2 m}\frac{d^2}{dx^2}\Psi$$

or, by defining the operator $(-h^2/8\pi^2 m)(d^2/dx^2)$ as $\widehat{T}$, we can rewrite the above as simply

$$\widehat{T}\,\Psi$$

which is much more compact. The above expression simply means "Take the group of mathematical operations indicated by $(-h^2/8\pi^2 m)(d^2/dx^2)$ and perform them on the wavefunction indicated by Ψ." Performance of an operation typically yields some expression, either a number or a function.

Example 10.2

For each of the following combinations of operator and function, write the complete mathematical operation and evaluate the expression.

$$\hat{O} = \frac{d}{dx} \qquad \hat{B} = \frac{d^2}{dx^2} \qquad \hat{S} = \exp(\ ) \text{ [raising 2.7182818 . . . to some power]}$$

$$\Psi_1 = 2x + 4 \qquad \Psi_2 = -3 \qquad \Psi_3 = \sin 4x$$

a. $\hat{S}\Psi_2$
b. $\hat{O}\Psi_1$
c. $\hat{B}\Psi_3$

Solution

a. $\hat{S}\Psi_2 = \exp(-3) = e^{-3} = 0.04978\ldots$

b. $\hat{O}\Psi_1 = \dfrac{d}{dx}(2x + 4) = 2$

c. $\hat{B}\Psi_3 = \dfrac{d^2}{dx^2}(\sin 4x) = \dfrac{d}{dx}(4 \cos 4x) = -16 \sin 4x$

In the examples above, the combination of operator and function yield an expression that could be mathematically evaluated. However, suppose the definitions are $\hat{L} = \ln(\ )$ and $\Psi = -10$. The expression $\hat{L}\Psi$ cannot be evaluated because logarithms of negative numbers do not exist. Not all operator/function combinations are mathematically possible, or yield meaningful results. Most operator/function combinations of interest to quantum mechanics *will* have meaningful results.

When an operator acts on a function, some other function is usually generated. There is a special type of operator/function combination that, when evaluated, produces some constant or group of constants *times the original function*. For instance, in Example 10.2c, the operator d^2/dx^2 is applied to the function sin 4x, and when the operator is evaluated, a constant times sin 4x is produced:

$$\frac{d^2}{dx^2}(\sin 4x) = \frac{d}{dx}(4 \cos 4x) = -16 \sin 4x$$

If we want to use the more concise symbolism for the operator and the function, the above expression can be represented as

$$\hat{B}\Psi = K\Psi \tag{10.2}$$

where K is a constant (in this case, −16). When an operator acts on a function and produces the original function multiplied by any constant (which may be 1 or sometimes 0), equation 10.2 is referred to as an *eigenvalue equation* and the constant K is called the *eigenvalue*. The function is called an *eigenfunction* of the operator. Not all functions are eigenfunctions of all operators. It is a rare occurrence for any random operator/function combination to yield an eigenvalue equation. In the example above, the eigenvalue equation is

$$\frac{d^2}{dx^2}(\sin 4x) = -16(\sin 4x)$$

where the parentheses are used to isolate the original function. The eigenfunction of the operator is sin 4x and the eigenvalue is −16.

Example 10.3

Which of the following operator/function combinations would yield eigenvalue equations? What are the eigenvalues of the eigenfunctions?

a. $\frac{d^2}{dx^2}\left(\cos\frac{x}{4}\right)$

b. $\frac{d}{dx}(e^{-4x})$

c. $\frac{d}{dx}(e^{-4x^2})$

Solution

a. Since

$$\frac{d^2}{dx^2}\left(\cos\frac{x}{4}\right) = -\frac{1}{16}\cos\frac{x}{4}$$

this is an eigenvalue equation with an eigenvalue of $-1/16$.

b. Since

$$\frac{d}{dx}(e^{-4x}) = -4(e^{-4x})$$

this is an eigenvalue equation with an eigenvalue of -4.

c. Since

$$\frac{d}{dx}(e^{-4x^2}) = -8x(e^{-4x^2})$$

this is not an eigenvalue equation because although the original function is reproduced, it is not multiplied by a constant. Instead, it is multiplied by another function, $-8x$.

Another postulate of quantum mechanics states that for every physical observable of interest, there is a corresponding operator. The *only* values of the observable that will be obtained in a single measurement must be eigenvalues of the eigenvalue equation constructed from the operator and the wavefunction (as shown in equation 10.2). This, too, is a central idea in quantum mechanics.

Two basic observables are position (usually—and arbitrarily—in the x direction) and the corresponding linear momentum. In classical mechanics, they are designated x and p_x. Many other observables are various combinations of these two basic observables. In quantum mechanics, the *position operator* $\hat{x}$ is defined by multiplying the function by the variable x:

$$\hat{x} = x\,\cdot \tag{10.3}$$

and the *momentum operator* $\widehat{p_x}$ (in the x direction) is defined in differential form as

$$\widehat{p_x} = -i\hbar\frac{\partial}{\partial x} \tag{10.4}$$

where i is the square root of -1 and $\hbar$ is Planck's constant divided by 2π, $h/2\pi$. The constant $\hbar$ is common in quantum mechanics. Note the definition of momentum as a derivative with respect to position, not with respect to time as with the classical definition. Similar operators exist for the y and z dimensions.

The postulate regarding eigenfunctions and eigenvalue equations gets more specific: the *only possible* values of the observables are those that are eigenvalues of the wavefunction when operated upon by the corresponding operator. No other values will be observed. Frequently, as we will see, this implies that many observables on the atomic scale are quantized. In addition, not all experimental quantities are determined by any given wavefunction. Rather, a given wavefunction is an eigenfunction of some operators (and so we can determine the values of those observables) but not an eigenfunction of other operators.

Example 10.4

What is the value of the momentum observable if the wavefunction Ψ is e^{-i4x}?

Solution

According to the postulate stated above, the momentum is equal to the eigenvalue produced by the expression

$$-i\hbar\frac{\partial}{\partial x}e^{-i4x}$$

When this expression is evaluated, we get

$$-i\hbar\frac{\partial}{\partial x}e^{-i4x} = (-i\hbar)(-i4)e^{-i4x} = -4\hbar e^{-i4x}$$

or, more succinctly,

$$-i\hbar\frac{\partial}{\partial x}e^{-i4x} = -4\hbar e^{-i4x}$$

where we have used $i \times i = -1$ to get the final expression. This is an eigenvalue equation with an eigenvalue of $-4\hbar$. Therefore, the value of the momentum from this wavefunction is $-4\hbar$. Numerically, $-4\hbar$ equals $(-4)(6.626 \times 10^{-34}\ \text{J·s})/2\pi = -4.218 \times 10^{-34}\ \text{J·s} = -4.218 \times 10^{-34}\ \text{kg·m}^2/\text{s}$.

In quantum mechanics, the eigenvalue equations that we will consider have real numbers as values of eigenvalues. Although we have already seen eigenfunctions and operators with the imaginary root i in them, when solving for the eigenvalue itself these imaginary parts must cancel out to yield a real number for the eigenvalue. *Hermitian operators* are operators that always have real (nonimaginary) numbers as eigenvalues (that is, K in equation 10.2 will always be a real number or a collection of constants that have real values). All operators that yield quantum mechanical observables are Hermitian operators, since in order to be observed a quantity must be real. (Hermitian operators are named after Charles Hermite, a nineteenth-century French mathematician.)

10.4 The Uncertainty Principle

Perhaps the most unusual part of quantum mechanics is the statement called the uncertainty principle. Occasionally it is called Heisenberg's uncertainty principle or the Heisenberg principle, after the German scientist Werner

Max Planck Institut fur Physik, courtesy AIP Emilio Segre Visual Archives

Figure 10.2 Werner Karl Heisenberg (1901–1976). Heisenberg's uncertainty principle completely changed the way science understands the limitations in the ability to measure nature. In World War II, Heisenberg was in charge of the German atomic bomb project, which he apparently purposely delayed to minimize the chance that the Nazis would develop an atomic bomb.

Heisenberg (Figure 10.2), who announced it in 1927. The *uncertainty principle* states that there are ultimate limits to how exact certain measurements can be. This idea was problematic for many scientists at the time, because science itself was concerned with finding specific answers to various questions. Scientists found that there were limits to how specific those answers could be.

Classically, if you know the position and momentum of a mass at any one time (that is, if you know those quantities *simultaneously*), you know everything about the motion of the mass because you know where it is and where it is going. If a tiny particle of mass has wave properties and its behavior is described by a wavefunction, how can we specify its position with a high degree of accuracy? According to the de Broglie equation, the de Broglie wavelength is related to a momentum, but how can we simultaneously determine the position and the momentum of something with wave behavior? As scientists developed a better understanding of subatomic matter, it was realized that there are some limits to the precision with which we can specify two observables simultaneously.

Heisenberg realized this and in 1927 announced his uncertainty principle. (The principle can be derived mathematically, so it is not a postulate of quantum mechanics. We will not cover the derivation here.) The uncertainty principle deals only with certain observables that might be measured simultaneously. Two of these observables are position x (in the x direction), and momentum p_x (also in the x direction). If the uncertainty in the position is given the symbol Δx and the uncertainty in the momentum is termed Δp_x, then Heisenberg's uncertainty principle is

$$\Delta x \cdot \Delta p_x \geq \frac{\hbar}{2} \tag{10.5}$$

where $\hbar$ is $h/2\pi$. Note the greater-than-or-equal-to sign in the equation. The uncertainty principle puts a *lower* bound on the uncertainty, not an upper bound. The units of position, m (meters), times the units of momentum, kg·m/s, equals the units on Planck's constant, J·s, which can also be written as kg·m^2/s.

Since the classical definition of momentum p is mv, equation 10.5 is sometimes written as

$$\Delta x \cdot m \cdot \Delta v \geq \frac{\hbar}{2} \tag{10.6}$$

where the mass m is assumed to be constant. Equation 10.6 implies that for large masses, the Δv and Δx can be so small that they are undetectable. However, for very small masses, Δx and Δp (or Δv) can be so *relatively* large that they can't be ignored.

Example 10.5

Determine the uncertainty in position, Δx, in the following cases:

a. A 1000-kg race car traveling at 100 meters per second, and v is known to within 1 meter per second.

b. An electron is traveling at 2.00×10^6 meters per second (the approximate velocity of an electron in Bohr's first quantum level) with an uncertainty in velocity of 1% of the true value.

Solution

a. For an auto traveling at 100 meters per second, an uncertainty of 1 meter per second is also a 1% uncertainty. The equation for the uncertainty principle becomes

$$\Delta x \cdot (1000 \text{ kg})(1 \text{ m/s}) \geq \frac{6.626 \times 10^{-34} \text{ J·s}}{2 \cdot 2 \cdot \pi}$$

where all of the values of the variables have been substituted into equation 10.5. Solving for Δx:

$$\Delta x \geq 5.27 \times 10^{-38} \text{ m}$$

You may want to verify not just the numbers but how the units work out. This minimum uncertainty is undetectable even using modern measurements of position and so this lower limit on the measurement would never be noticed.

b. For a small electron, using the same equation but different numbers:

$$\Delta x(9.109 \times 10^{-31} \text{ kg})(2.00 \times 10^{4} \text{ m/s}) \geq \frac{6.626 \times 10^{-34} \text{ J·s}}{2 \cdot 2 \cdot \pi}$$

where we have used the mass of the electron and, for 1% of the velocity of the electron, $[0.01(2.00 \times 10^{6}) = 2.00 \times 10^{4}]$. Solving for Δx:

$$\Delta x \geq 2.89 \times 10^{-9} \text{ m} \geq 2.89 \text{ nm} \geq 28.9 \text{ Å}$$

The uncertainty in the position of the electron is at least 3 nanometers, several times larger than atoms themselves. It would be easy to notice experimentally that one couldn't pin down the position of an electron to within 3 nm!

The above example illustrates that the idea of uncertainty cannot be ignored *at the atomic level.* Certainly, if the velocity were known to lower precision, say, to one part in ten, the corresponding minimum uncertainty in the *position* would be lower. But the uncertainty principle states mathematically that as one goes up, the other goes down, and neither can be zero for simultaneous determinations. The uncertainty principle does not address a maximum uncertainty, so the uncertainty can be (and usually is) larger. But some measurements have a fundamental limit to how exactly they can be determined simultaneously with other observables.

Finally, position and momentum are not the only two observables whose uncertainties are related through an uncertainty principle. (In fact, another mathematical form of the uncertainty principle is expressed in terms of the operators for the observables, like equations 10.3 and 10.4, and not the observable values themselves.) There are many such combinations of observables, like multiple components of angular momentum. There are also combinations of observables for which an uncertainty-principle relationship does not apply, implying that those observables *can* be known simultaneously to any level of precision. Position and momentum are commonly used to introduce this concept, but the concept is not limited to x and p_x.

10.5 The Born Interpretation of the Wavefunction; Probabilities

What we have are two seemingly incompatible ideas. One is that the behavior of an electron is described by a wavefunction. The other is that the uncertainty principle limits the certainty with which one can measure various combinations of observables, like position and momentum. How can we discuss the motion of electrons in any detail at all?

The German scientist Max Born (Figure 10.3) interpreted the wavefunc-


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Figure 10.3 Max Born (1882–1970). His interpretation of the wavefunction as a probability rather than an actuality changed the common understanding of quantum mechanics.

tions in terms that accepted the uncertainty principle, and the *Born interpretation* is generally considered to be the correct way of thinking of Ψ. Because of the uncertainty principle, Born suggested that we not think of Ψ as indicating a *specific* path of an electron. It is very difficult to establish *absolutely* that a particular electron is in a particular place at a particular time. Rather, over a long period of time, the electron has a certain probability of being in a certain region. The probability can be determined from the wavefunction Ψ. Specifically, Born stated that the probability P of an electron being in a certain region between points a and b in space is

$$P = \int_b^a \Psi^*\Psi \, d\tau \tag{10.7}$$

where Ψ^* is the *complex conjugate* of Ψ (where every i in the wavefunction is replaced with $-i$), $d\tau$ is the infinitesimal of integration covering the dimensional space of interest [dx for one dimension, ($dx\,dy$) for two dimensions, ($dx\,dy\,dz$) for three dimensions, and ($r^2 \sin\theta\, dr\, d\theta\, d\phi$) for spherical polar coordinates], and the integral is evaluated over the interval of interest (between points a and b, in this case). Note that Ψ^* and Ψ are simply being multiplied together (which is sometimes written as $|\Psi|^2$). The operation of multiplication is assumed the way the integrand (the part inside the integral sign) is written. The Born interpretation also requires that a probability be evaluated over a definite *region*, not a specific point, in space. Thus, we should think of Ψ as an indicator of the *probability* that the electron will be in a certain region of space.

The Born interpretation affects the entire meaning of quantum mechanics. Instead of Ψ giving the exact location of an electron, it will provide only the probability of the location of an electron. For those who were content with understanding that they could calculate *exactly* where matter was in terms of Newton's laws, this interpretation was a problem since it denied them the ability to state *exactly* how matter was behaving. All they could do was state the *probability* that matter was behaving that way. Ultimately, the Born interpretation was accepted as the proper way to consider wavefunctions.

Example 10.6

Using the Born interpretation, for an electron having a one-dimensional wavefunction $\Psi = \sqrt{2}\sin \pi x$ in the range $x = 0$ to 1, what are the following probabilities?

a. The probability that the electron is in the first half of the range, from $x = 0$ to 0.5

b. The probability that the electron is in the middle half of the range, from $x = 0.25$ to 0.75

Solution

For both parts, one needs to solve the following integral:

$$P = \int_b^a (\sqrt{2}\sin \pi x)^*(\sqrt{2}\sin \pi x)\, dx$$

but between different initial and final limits. Since the wavefunction is a real function, the complex conjugate does not change the function, and the integral becomes

$$P = 2\int_b^a \sin^2 \pi x \, dx$$

where the constant 2 has been taken outside the integral sign. This integral has a known solution. It is

$$\int_b^a \sin^2 \pi x \, dx = \frac{x}{2} - \frac{1}{4\pi} \sin 2\pi x \Big|_b^a$$

where we have substituted into the general form of the integral for the constants in this particular example (you should verify this substitution yourself).

a. Evaluating for the region $x = 0$ to 0.5:

$$P = 2[0.25 - 0 - (0 - 0)]$$

$$P = 2(0.25)$$

$$P = 0.50$$

which as a percentage is 50%. This should, perhaps, be expected: in one-half of the region of interest, the probability of the electron being there is one half, or 50%.

b. For $x = 0.25$ to 0.75:

$$P = 2\left[0.375 - \frac{1}{4\pi}(-1) - \left(0.125 - \frac{1}{4\pi}1\right)\right]$$

$$P = 2(0.409)$$

$$P = 0.818$$

which means that the probability of finding the electron in the middle half of this region is 81.8%—much greater than half! This result is a consequence of the wavefunction being a sine function. It also illustrates some of the more unusual predictions of quantum mechanics.

The Born interpretation makes obvious the necessity of wavefunctions being bounded and single-valued. If a wavefunction is not bounded, it approaches infinity. Then the integral over that space, the probability, is infinite. Probabilities cannot be infinite. Since probability of existence represents a physical observable, it must have a specific value; therefore, Ψ's (and their squares) must be single-valued.

Because the wavefunction in this last example does not depend on time, its probability distribution also does not depend on time. This is the definition of a *stationary state*: a state whose probability distribution, related to $|\Psi(x)|^2$ by the Born interpretation, does not vary with time.

10.6 Normalization

The Born interpretation suggests that there should be another requirement for acceptable wavefunctions. If the probability for a particle having wavefunction Ψ were evaluated over the entire space in which the particle exists, then the probability should be equal to 1, or 100%. In order for this to be the case, wavefunctions are expected to be *normalized*. In mathematical terms, a wavefunction is normalized if and only if

$$\int_{-\infty}^{+\infty} \Psi^*\Psi \, d\tau = 1 \qquad \textbf{(10.8)}$$

The limits $+\infty$ and $-\infty$ are conventionally used to represent "all space," although the entire space of a system may not actually extend to infinity in both directions. The integral's limits would be modified to represent the limits of the space a particle inhabits. What equation 10.8 usually means is that wavefunctions must be multiplied by some constant so that the area under the curve of $\Psi^*\Psi$ is equal to 1. According to the Born interpretation of Ψ, normalization also guarantees that the probability of a particle existing in all space is 100%.

Example 10.7

Assume that a wavefunction for a system exists and is $\Psi(x) = \sin(\pi x/2)$, where x is the only variable. If the region of interest is from $x = 0$ to $x = 1$, normalize the function.

Solution

By equation 10.8, the function must be multiplied by some constant so that $\int_0^1 \Psi^*\Psi\, dx = 1$. Note that the limits are 0 to 1, not $-\infty$ to $+\infty$, and that $d\tau$ is simply dx for this one-dimensional example. Let us assume that Ψ is multiplied by some constant N:

$$\Psi \longrightarrow N\Psi$$

Substituting for Ψ into the integral, we get

$$\int_0^1 (N\Psi)^*(N\Psi)\, dx = \int_0^1 N^*N\left(\sin\frac{\pi x}{2}\right)^*\left(\sin\frac{\pi x}{2}\right) dx$$

Since N is a constant, it can be pulled out of the integral, and since this sine function is a real function, the * has no effect on the function (recall it changes every i to $-i$, but there is no imaginary part of the function in this example). Therefore, we get

$$\int_0^1 N^*N\left(\sin\frac{\pi x}{2}\right)^*\left(\sin\frac{\pi x}{2}\right) dx = N^2\int_0^1 \sin^2\frac{\pi x}{2}\, dx$$

Normalization requires that this expression equal 1:

$$N^2\int_0^1 \sin^2\frac{\pi x}{2}\, dx = 1$$

The integral in this expression has a known form and it can be solved, and the definite integral from the limits 0 to 1 can be evaluated. Referring to the table of integrals in Appendix 1, we find that

$$\int \sin^2 bx\, dx = \frac{x}{2} - \frac{1}{4b}\sin 2bx$$

In our case, $b = \pi/2$. Evaluating the integral between the limits, we find that the normalization requirement simplifies to

$$N^2\left(\frac{1}{2}\right) = 1$$

Solving for N:

$$N = \sqrt{2}$$

where the positive square root is assumed. The correctly normalized wavefunction is therefore $\Psi(x) = \sqrt{2}[\sin(\pi x/2)]$.

The wave*function* in the above example has not changed. It is still a sine function. However, it is now multiplied by a constant so that the normalization condition is satisfied. The normalization constant does not affect the shape of the function. It only imposes a scaling factor on the amplitude—a very convenient scaling factor, as we will find. For the remainder of this text, all wavefunctions must be or will be normalized unless stated otherwise.

Example 10.8

The wavefunction $\Psi = \sqrt{2}\sin \pi x$ is valid for the range $x = 0$ to 1. Verify that an electron has a 100% probability of existing in this range, thus verifying that this wavefunction is normalized.

Solution

Evaluate the expression

$$P = 2\int_0^1 \sin^2 \pi x \, dx$$

and show that it is identically equal to 1. This integral has a known solution, and substituting that solution, we get

$$P = 2\left[\frac{x}{2} - \frac{1}{4\pi}\sin(2\pi x)\Big|_0^1\right]$$

$$= 2\left[\frac{1}{2} - 0 - \left(\frac{0}{2} - 0\right)\right]$$

where the limits have been substituted into the expression for the integral. Solving:

$$P = 1$$

which verifies that the wavefunction is normalized. Thus, from the Born interpretation, the probability of finding the particle in the range $x = 0$ to 1 is exactly 100%.

10.7 The Schrödinger Equation

One of the most important ideas in quantum mechanics is the Schrödinger equation, which deals with the most important observable: energy. A change in the energy of an atomic or molecular system is usually one of the easiest things to measure (usually by spectroscopic methods, as discussed in the previous chapter), so it is important that quantum mechanics be able to predict energies.

In 1925 and 1926, Erwin Schrödinger (Figure 10.4) brought together many of the ideas presented in Chapter 9 as well as in earlier sections of this chapter, ideas like operators and wavefunctions. The Schrödinger equation is based on the Hamiltonian function (section 9.2), since these equations naturally produce the total energy of the system:

$$E_{\text{tot}} = K + V$$

where K represents the kinetic energy and V is the potential energy. We will start with a one-dimensional system. Kinetic energy, energy of motion, has a


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Figure 10.4 Erwin Schrödinger (1887–1961). Schrödinger proposed an expression of quantum mechanics that was different from but equivalent to Heisenberg's. His expression is useful because it expresses the behavior of electrons in terms of something we understand—waves. The Schrödinger equation is the central equation of quantum mechanics.

specific formula from classical mechanics. In terms of linear momentum p_x, kinetic energy is given by

$$K = \frac{p_x^2}{2m}$$

Schrödinger, however, thought in terms of operators acting on wavefunctions, and so he rewrote the Hamiltonian function in terms of operators. Using the definition of the momentum operator,

$$\widehat{p_x} = -i\hbar\frac{\partial}{\partial x}$$

and supposing that the potential energy is a function of *position* (that is, a function of x) and so can be written in terms of the position operator,

$$\hat{x} = x\,\cdot$$

Schrödinger substituted into the expression for the total energy to derive an operator for energy named (for obvious reasons) the *Hamiltonian operator* $\widehat{H}$:

$$\widehat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \widehat{V}(x) \qquad \textbf{(10.9)}$$

This operator $\widehat{H}$ operates on a wavefunction Ψ and the eigenvalue corresponds to the total energy of the system E:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \widehat{V}(x)\right]\Psi = E\Psi \qquad \textbf{(10.10)}$$

Equation 10.10 is known as the *Schrödinger equation* and is a very important equation in quantum mechanics. Although we have placed certain restrictions on wavefunctions (continuous, single-valued, and so on), up to now there has been no requirement that an acceptable wavefunction satisfy any *particular* eigenvalue equation. However, if Ψ is a stationary state (that is, if its probability distribution does not depend on time), it should also satisfy the Schrödinger equation. Also note that equation 10.10 does not include the variable for time. Because of this, equation 10.10 is more specifically referred to as the *time-independent Schrödinger equation.* (The time-*dependent* Schrödinger equation will be discussed near the end of the chapter and represents another postulate of quantum mechanics.)

Although the Schrödinger equation may be difficult to accept at first, it works: when applied to ideal and even real systems, it yields the values for the energies of the systems. For example, it correctly predicts changes in energy of the hydrogen atom, which is a system that had been studied for decades before Schrödinger's work. Quantum mechanics, however, uses a new mathematical tool—the Schrödinger equation—for predicting observable atomic phenomena. Because the values of atomic and molecular observables are properly predicted by using the Schrödinger equation and wavefunctions, they are considered the proper way of thinking about atomic phenomena. The behavior of electrons is described by a wavefunction. The wavefunction is used to determine all properties of the electrons. Values of these properties can be predicted by operating on the wavefunction with the appropriate operator. The appropriate operator for predicting the energy of the electron is the Hamiltonian operator.

To see how the Schrödinger equation works, the following example illustrates how the Hamiltonian operates on a wavefunction.

Example 10.9

Consider an electron confined to some finite system. The state of the electron is described by the wavefunction $\Psi = \sqrt{2}\sin k\pi x$, where k is some constant. Assume that the potential energy is zero, or $V(x) = 0$. What is the energy of the electron?

Solution

Since the potential energy is zero, the electron has only kinetic energy. The Schrödinger equation reduces to

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right]\Psi = E\Psi$$

We rewrite it as

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = E\Psi$$

We need to evaluate the second derivative of Ψ, multiply it by the appropriate set of constants, and regenerate the original wavefunction and find out what constant E is multiplying Ψ. That E is the energy of the electron. Evaluating the second derivative:

$$\frac{\partial^2}{\partial x^2}(\sqrt{2}\sin k\pi x) = -k^2\pi^2(\sqrt{2}\sin k\pi x) = -k^2\pi^2\Psi$$

Therefore, we can substitute $-k^2\pi^2\Psi$ into the left side of the Schrödinger equation:

$$-\frac{\hbar^2}{2m}(-k^2\pi^2\Psi) = \frac{\hbar^2k^2\pi^2}{2m}\Psi$$

From this expression, we should see that the energy eigenvalue has the expression

$$E = \frac{k^2\hbar^2\pi^2}{2m}$$

The kinetic energy part of the Hamiltonian has a similar form for all systems (although it may be described using different coordinate systems, as we will see in rotational motion). However, the potential energy operator $\hat{V}$ depends on the system of interest. In the examples of systems using the Schrödinger equation, different expressions for the potential energy will be used. What we will find is that the exact form of the potential energy determines if the second-order differential equation is exactly solvable. If it is, we say that we have an *analytic* solution. In many cases, it is *not* solvable analytically and must be approximated. The approximations can be very good, good enough for their predictions to agree with experimental determinations. However, exact solutions to the Schrödinger equation, along with specific predictions of various observables like energy, are necessary to illustrate the true usefulness of quantum mechanics.

Among the quantum mechanical operators presented so far, the Hamiltonian is probably the most important one. As a summary, a short list of quantum-mechanical operators and their classical counterparts is provided in Table 10.1.

Table 10.1 Operators for various observables and their classical counterparts[a]

Observable	Operator	Classical counterpart
Position	$\hat{x} = x \cdot$ And so forth for coordinates other than x	x
Momentum (linear)	$\widehat{p_x} = -i\hbar\frac{\partial}{\partial x}$ And so forth for coordinates other than x	$p_x = mv_x$
Momentum (angular)	$\widehat{L_x} = -i\hbar\left(\hat{y}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial y}\right)$	$L_x = yp_z - zp_y$
Kinetic energy, 1-D[b]	$\hat{K} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$	$K = \frac{1}{2}mv_x^2 = \frac{p_x^2}{2m}$
Kinetic energy, 3-D[b]	$\hat{K} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$	$K = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$ $= \frac{p_x^2 + p_y^2 + p_z^2}{2m}$
Potential energy:		
Harmonic oscillator	$\hat{V} = \frac{1}{2}kx^2 \cdot$	$V = \frac{1}{2}kx^2$
Coulombic	$\hat{V} = \frac{q_1 \cdot q_2}{4\pi\epsilon_0 r} \cdot$	$V = \frac{q_1 \cdot q_2}{4\pi\epsilon_0 r}$
Total energy	$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \hat{V}$	$H = \frac{p^2}{2m} + V$

[a] Operators expressed in x, y, and/or z are Cartesian operators; operators expressed in r, θ, and/or ϕ are spherical polar operators.

[b] The kinetic energy operator is also symbolized by $\hat{T}$.

10.8 An Analytic Solution: The Particle-in-a-Box

Very few systems have analytic solutions (that is, solutions that have a specific mathematical form, either a number or an expression) to the Schrödinger equation. Most of the systems having analytic solutions are defined ideally, much as an ideal gas is defined. This should not be a cause for despair. The few ideal systems whose exact solutions can be determined have applications in the real world, so they are not wasted on ideality! Several of these systems were recognized by Schrödinger himself as he developed his equation.

The first system for which there is an analytic solution is a particle of matter stuck in a one-dimensional "prison" whose walls are infinitely high barriers. This system is called the *particle-in-a-box*. The infinitely high barriers correspond to potential energies of infinity; the potential energy inside the box itself is defined as zero. Figure 10.5 illustrates the system. Arbitrarily, we are setting one side of the box at $x = 0$ and the other at some length a. Inside this box the potential energy is 0. Outside, the potential energy is infinity.

The analysis of this system using quantum mechanics is similar to the analysis that we will apply to every system. First, consider the two regions where the potential energy is infinity. According to the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \infty\right]\Psi = E\Psi$$

must hold true for $x < 0$ and $x > a$. The infinity presents a problem, and in this case the way to eliminate infinity is to multiply it by zero. Thus, Ψ must be identically zero in the regions $x < 0$ and $x > a$. It does not matter

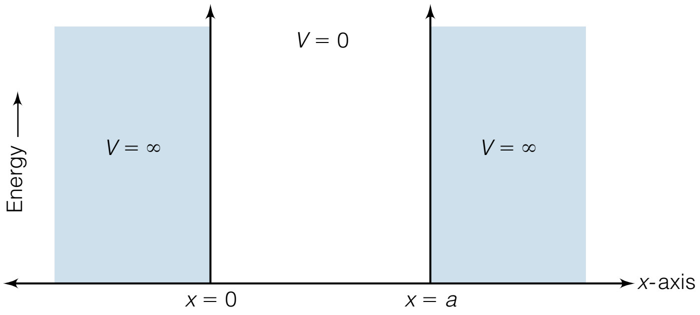

Figure 10.5 The particle-in-a-box is the simplest ideal system that is treated by quantum mechanics. It consists of a region between $x = 0$ and $x = a$ (some length) where the potential energy is zero. Outside of this region ($x < 0$ or $x > a$), the potential energy is ∞, so any particle in the box will not be present outside the box.

what the eigenvalues for the energy are, because with Ψ identically zero, by the Born interpretation the particle has a zero probability of being in those regions.

Consider the region where x ranges from 0 to a. The potential energy is defined as zero in this region and so the Schrödinger equation becomes

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right]\Psi = E\Psi$$

which is a second-order differential equation. This differential equation has a known analytic solution. That is, functions are known that can be substituted into the above second-order differential equation to satisfy the equality. The most general form of the solution to the above differential equation is

$$\Psi = A\cos kx + B\sin kx$$

where A, B, and k are constants to be determined by the conditions of the system.*

Since we know the form of Ψ, we can determine the expression for E by substituting Ψ into the Schrödinger equation and evaluating the second derivative. It becomes

$$E = \frac{k^2\hbar^2}{2m}$$

Example 10.10

Show that the expression for the energy of a particle in a box is $E = k^2\hbar^2/2m$.

Solution

All that needs to be done is to substitute the wavefunction $\Psi = A\cos kx + B\sin kx$ into the Schrödinger equation, remembering that the potential energy V is zero. We get

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*Acceptable solutions can also be written in the form

$$\Psi = A'e^{ikx} + B'e^{-ikx}$$

This form is related to $\Psi = A\cos kx + B\sin kx$ via Euler's theorem, which states that $e^{i\theta} = \cos\theta + i\sin\theta$.

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}(A\cos kx + B\sin kx) = \frac{-\hbar^2}{2m}\frac{\partial}{\partial x}(kA\cos kx - kB\sin kx)$$

$$= \frac{-\hbar^2}{2m}(-k^2A\cos kx - k^2B\sin kx)$$

Factoring $-k^2$ out of the terms in parentheses, we can get our original wavefunction back:

$$= \frac{-(-k^2)\hbar^2}{2m}(A\cos kx + B\sin kx)$$

The two negative signs cancel, and the collection of terms multiplying the wavefunction are all constants. We have thus shown that operation of the Hamiltonian operator on this wavefunction yields an eigenvalue equation; the eigenvalue is the energy of a particle having that wavefunction:

$$E = \frac{k^2\hbar^2}{2m}$$

Note that at this point, we have no idea what the constant k is.

In the above example, the wavefunction determined is deficient in a few respects, specifically the identities of several constants. Up to this point, nothing has constrained those constants to any particular value. Classically, the constants can have any value, indicating that the energy can have any value. However, quantum mechanics imposes certain restrictions on allowed wavefunctions.

The first requirement of the wavefunction is that it must be continuous. Since we recognize that the wavefunction in the regions $x < 0$ and $x > a$ must be zero, then the wavefunction's value at $x = 0$ and $x = a$ must be zero. This is certainly true when approaching these limits of x from *outside* the box, but the continuity of the wavefunction requires that this must also hold when approaching these limits from *inside* the box. That is, $\Psi(0)$ must equal $\Psi(a)$ which must equal zero. This requirement, that the wavefunction must be a certain value at the boundaries of the system, is called a *boundary condition.**

The boundary condition $\Psi(0)$ is applied first: since $x = 0$, the wavefunction becomes

$$\Psi(0) = 0 = A\cos 0 + B\sin 0$$

Since $\sin 0 = 0$, the second term places no restriction on the possible value(s) of B. However, $\cos 0 = 1$, and this is a problem unless $A = 0$. So, in order to satisfy this first boundary condition, A must be zero, meaning that the only acceptable wavefunctions are

$$\Psi(x) = B\sin kx$$

Now we apply the other boundary condition: $\Psi(a) = 0$. Using the wavefunction from above:

$$\Psi(a) = 0 = B\sin ka$$

where a has been substituted for x. We cannot require that B equal zero. If it

---

*Boundary conditions are also apparent for some classical waves. For example, a vibrating guitar string has a wave motion whose amplitude is zero at the ends, where the string is tied down.

were, then Ψ would be zero between 0 and a, and then it would be zero everywhere and the particle would not exist anywhere. We reject that possibility, since the particle's existence is unquestioned. In order for the wavefunction to equal zero at $x = a$, the value of sin ka *must* be zero:

$$\sin ka = 0$$

When is sin ka equal to 0? In terms of radians, this occurs when ka equals 0, π, 2π, 3π, 4π, . . . or at all integral values of π. We reject the value 0 because sin *0* equals 0 and so the wavefunction would not exist anywhere. We thus have the following restriction on the argument of the sine function:

$$ka = n\pi \qquad n = 1, 2, 3, \ldots$$

Solving for k,

$$k = \frac{n\pi}{a}$$

where n is a positive integer. Although there is no mathematical reason n can't be a negative integer, use of negative integers adds nothing new to the solution, so they are ignored. This will not always be the case.

Having an expression for k allows us to rewrite both the wavefunction and the expression for the energies:

$$\Psi(x) = B \sin \frac{n\pi x}{a}$$

$$E = \frac{n^2\pi^2\hbar^2}{2ma^2} = \frac{n^2h^2}{8ma^2}$$

where the definition for $\hbar$ has been substituted in the last expression for energy. The energy values depend on some constants and on n, which is restricted to positive integer values. This means that the energy cannot have just any value; it can have only values determined by h, m, a, and—most importantly—n. The energy of the particle in the box is *quantized,* since the energy value is restricted to having only certain values. The integer n is called a *quantum number.*

The determination of the wavefunction is not complete. It must be normalized. It is assumed to be multiplied by some constant N such that

$$\int_0^a (N\Psi)^*(N\Psi)\, dx = 1$$

The limits on the integral are 0 to a because the only region of interest for the nonzero wavefunction is from $x = 0$ to $x = a$. The infinitesimal $d\tau$ is simply dx.

We will assume that the normalization constant is part of the constant B that multiplies the sine part of the wavefunction. The integral to be evaluated is

$$\int_0^a \left(N \sin \frac{n\pi x}{a}\right)^* \left(N \sin \frac{n\pi x}{a}\right) dx = 1$$

The complex conjugate does not change anything inside the parentheses, since everything is a real number or real function. A function similar to this was evaluated in Example 10.7. By following the same procedure as in that example (and you should verify that the procedure has the following result), we find that $N = \sqrt{2/a}$. Since both the wavefunction and the energy are dependent on some quantum number n, they are usually given a subscript n, like Ψ_n and E_n, to indicate this dependence. The acceptable wavefunctions for a one-dimensional particle-in-a-box are written as

$$\Psi_n(x) = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}, \qquad n = 1, 2, 3, 4, \ldots \tag{10.11}$$

The quantized energies of the particles in this box are

$$E_n = \frac{n^2h^2}{8ma^2} \tag{10.12}$$

What do these wavefunctions look like? Figure 10.6 shows plots of the first few wavefunctions. All of them go to zero at the sides of the box, as required by the boundary conditions. All of them look like simple sine functions (which is what they are) with positive and negative values.

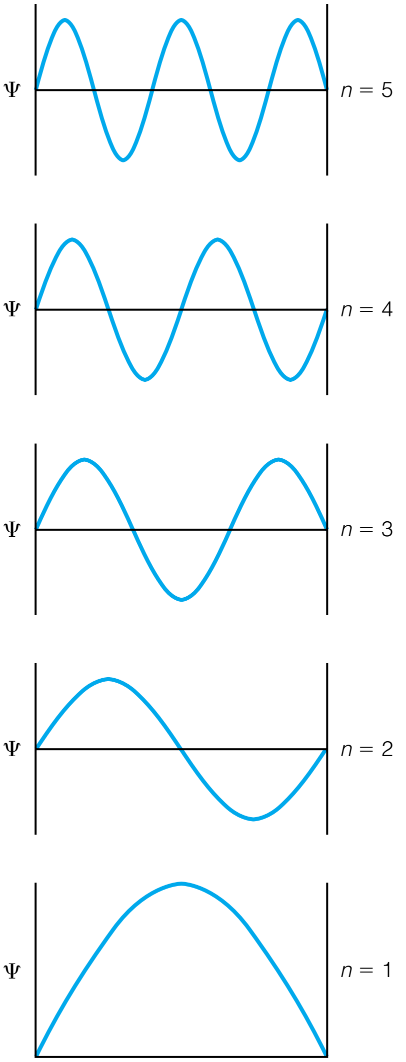


Figure 10.6 Plots of the first few quantum-mechanically acceptable particle-in-a-box wavefunctions.

Example 10.11

Determine the wavefunctions and energies of the first four levels of an electron in a box having a width of 10.0 Å; that is, a = 10.0 Å = 1.00×10^{-9} m.

Solution

Using equation 10.11, the expressions of the wavefunctions are straightforward:

$$\Psi_1(x) = \sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}$$

$$\Psi_2(x) = \sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a}$$

$$\Psi_3(x) = \sqrt{\frac{2}{a}}\sin\frac{3\pi x}{a}$$

$$\Psi_4(x) = \sqrt{\frac{2}{a}}\sin\frac{4\pi x}{a}$$

Using equation 10.12, the energies are

$$E_1 = \frac{1^2h^2}{8m_ea^2} = \frac{1^2(6.626\times10^{-34}\ \text{J}\cdot\text{s})^2}{8(9.109\times10^{-31}\ \text{kg})(1.00\times10^{-9}\ \text{m})^2} = 6.02\times10^{-20}\ \text{J}$$

$$E_2 = \frac{2^2h^2}{8m_ea^2} = \frac{2^2(6.626\times10^{-34}\ \text{J}\cdot\text{s})^2}{8(9.109\times10^{-31}\ \text{kg})(1.00\times10^{-9}\ \text{m})^2} = 24.1\times10^{-20}\ \text{J}$$

$$E_3 = \frac{3^2h^2}{8m_ea^2} = \frac{3^2(6.626\times10^{-34}\ \text{J}\cdot\text{s})^2}{8(9.109\times10^{-31}\ \text{kg})(1.00\times10^{-9}\ \text{m})^2} = 54.2\times10^{-20}\ \text{J}$$

$$E_4 = \frac{4^2h^2}{8m_ea^2} = \frac{4^2(6.626\times10^{-34}\ \text{J}\cdot\text{s})^2}{8(9.109\times10^{-31}\ \text{kg})(1.00\times10^{-9}\ \text{m})^2} = 96.4\times10^{-20}\ \text{J}$$

The exponents on the magnitudes of the energies have been intentionally kept the same, 10^{-20}, to illustrate how the energy changes with quantum number n. Note that whereas the wavefunctions depend on n, the energies depend on n^2. You should verify that the units in the above expression do yield units of joules as the unit of energy.

10.9 Average Values and Other Properties

There are other common observables in addition to energy. One could operate on the wavefunction with the position operator, $\hat{x}$, which is simply multiplication by the coordinate x, but multiplying the sine functions of the particle-in-a-box by the coordinate x does not yield an eigenvalue equation. *The Ψ's of equation 10.11 are not eigenfunctions of the position operator.*

This should not be cause for concern. The postulates of quantum mechanics do not require that acceptable Ψ's be eigenfunctions of the position operator. (They require a special relationship with the Hamiltonian operator, but not any other.) This does not imply that we cannot extract *any* information about the position from the wavefunction, only that we cannot determine eigenvalue observables for position. The same is true for other operators, like momentum.

The next postulate of quantum mechanics that we will deal with concerns observables like this. It is postulated that although *specific* values of some observables may not be forthcoming from all wavefunctions, *average* values of these observables might be determined. In quantum mechanics, the *average value* or *expectation value* $\langle A \rangle$ of an observable A whose operator is $\hat{A}$ is given by the expression

$$\langle A \rangle = \int_b^a \Psi^* \hat{A} \Psi \, d\tau \tag{10.13}$$

Equation 10.13, which is another postulate of quantum mechanics, assumes that the wavefunction is normalized. If it is not, the definition of an average value expands slightly to

$$\langle A \rangle = \frac{\displaystyle\int_b^a \Psi^* \hat{A} \Psi \, d\tau}{\displaystyle\int_b^a \Psi^* \Psi \, d\tau}$$

An average value is just what it says: if one were to take repeated measurements of the same quantity and average them together, what would that average value be? Quantum mechanically, if one were able to take an infinite number of measurements, the average value would be the average of all of those infinite measurements.

What is the difference between an average value as determined by equation 10.13 and the single eigenvalue of an observable determined from an eigenvalue equation? For some observables, there is no difference. If you know that a particle-in-a-box is in a certain state, it has a certain wavefunction. According to the Schrödinger equation, you know its exact energy. The average value of that energy is the same as its instantaneous energy, because while in the state described by that wavefunction, the energy does not change. However, some observables cannot be determined from all wavefunctions using an eigenvalue equation. The wavefunctions for the particle-in-a-box, for example, are not eigenfunctions of the position or momentum operators. We cannot determine instantaneous, exact values for these observables. But we *can* determine average values for them. (Recognize that although the uncertainty principle denies us the opportunity to know the *specific* values of the position and momentum of any particle simultaneously, there is no restriction on knowing *average* values of the position or the momentum.)

Example 10.12

Determine $\langle x \rangle$, the average value of the position of an electron having the lowest energy level ($n = 1$) in a particle-in-a-box.

Solution

By definition, the average value of the position $\langle x \rangle$ for the lowest energy level is

$$\langle x \rangle = \int_0^a \left(\sqrt{\frac{2}{a}} \sin \frac{\pi x}{a} \right)^* \cdot x \cdot \left(\sqrt{\frac{2}{a}} \sin \frac{\pi x}{a} \right) dx$$

where all of the functions inside the integral sign are being multiplied together, the limits of the system are 0 to a, and $d\tau$ is dx. Because the function is real, the complex conjugate doesn't change anything and the expression becomes (because multiplication is commutative)

$$\langle x \rangle = \frac{2}{a} \int_0^a x \cdot \sin^2 \frac{\pi x}{a} \, dx$$

This integral also has a known solution (see Appendix 1). On solving, this expression becomes

$$\frac{2}{a} \left(\frac{x^2}{4} - \frac{xa}{4\pi} \sin \frac{2\pi x}{a} - \frac{a^2}{8\pi^2} \cos \frac{2\pi x}{a} \right) \Big|_0^a$$

When this is evaluated, the average value for the position is

$$\langle x \rangle = \frac{a}{2}$$

Thus, this particle having the given wavefunction has an average position in the middle of the box.

The above example illustrates two things. First, average values *can* be determined for observables that cannot be determined using an eigenvalue equation (which a postulate of quantum mechanics requires of its observables); and second, average values should make sense. It would be expected that for a particle bouncing back and forth in a box, its average position be the middle of the box. It should spend as much time on one side as on the other, so its average position would be right in the middle. This is what equation 10.13 provides, at least in this case: an intuitively reasonable value. There are many examples in quantum mechanics where a reasonable average is produced, albeit from a different argument than classical mechanics. This simply reinforces the applicability of quantum mechanics. The average value of the position of the particle in a box is $a/2$ for *any* value of the quantum number n. Evaluate, as an exercise, the average value of the position observable for

$$\Psi_3(x) = \sqrt{\frac{2}{a}} \sin \frac{3\pi x}{a}$$

where the subscript on Ψ indicates that this wavefunction has the quantum number $n = 3$. The solution for the integral used for the average value shows that the quantum number n, whatever it is, has no effect in the determination of $\langle x \rangle$. (These conclusions only apply to stationary states of the particle-in-a-box. If the wavefunctions are not stationary states, $\langle x \rangle$ and other average values would not necessarily be intuitively consistent with classical mechanics.)

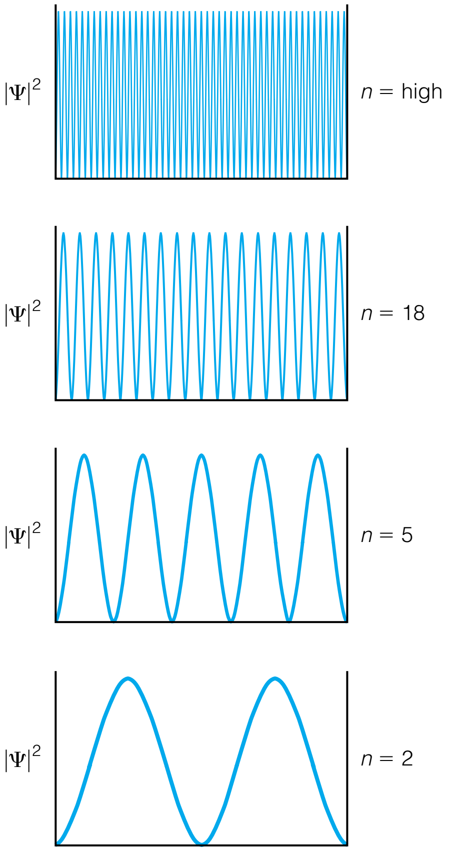


Figure 10.7 The plots of $|\Psi|^2$ illustrate the correspondence principle: for large quantum numbers, quantum mechanics begins to approximate classical mechanics. At large n, the particle-in-a-box looks as if the particle were present in all regions of the box with equal probability.

Other properties can also be determined from Ψ for the particle-in-a-box. We point them out because they are properties that can be determined for all of the systems that will be considered. The energy of a particle having a particular wavefunction has already been discussed. Example 10.12 shows that the observable position can be determined, although only as an average value. The average value of the (one-dimensional) momentum can also be determined using the momentum operator. Figure 10.6, which shows plots of the first few wavefunctions of the particle in a box, illustrates other features of the wavefunctions. For example, there are positions in the box where the wavefunction should be identically zero: at the limits of the box, $x = 0$ and $x = a$, in all cases. For Ψ_1, those are the only positions where $\Psi = 0$. For larger values of the quantum number n, there more positions where the wavefunction goes to zero. For Ψ_2, there is one more position in the center of the box. For Ψ_3, there are two additional positions along with the boundaries; for Ψ_4, there are three. A *node* is a point at which the wavefunction is exactly zero. Not including the boundaries, for Ψ_n there are $n - 1$ nodes in the wavefunction.

More information is available from a plot of $\Psi^*\Psi$, which is related to the probability density that a particle exists at any particular point in the box (although probability densities are evaluated only for *regions* of space, not individual points in space).[†] Such plots for some particle-in-a-box wavefunctions are shown in Figure 10.7. These plots imply that a particle has a varying probability of existing in different regions of the box. At the boundaries and at every node, the probability of the particle existing at that point is exactly zero. At the boundaries this causes no problem, but at the nodes? How can a particle be on one side of a node and also the other without having any probability of existing at the node itself? That's like being inside a room and then outside a room and never being in the doorway. This is the first of many oddities in the interpretation of quantum mechanics.

The other thing to notice about the plot of probability densities is that as one goes to higher and higher quantum numbers, the plot of $|\Psi|^2$ can be approximated as some constant probability. This is an example of the *correspondence principle:* at sufficiently high energies, quantum mechanics agrees with classical mechanics. The correspondence principle was first stated by Niels Bohr and puts classical mechanics in its proper place: a very good first approximation when applied to atomic systems in high-energy or high-quantum-number states (and, for all practical purposes, absolutely correct when applied to macroscopic systems).

Before we leave this section, we point out that this "ideal" system does have an application in the real world. There are many examples of large organic molecules that have alternating single and double bonds, a so-called conjugated double bond system. In such cases, the electrons in the double bonds are considered to move somewhat freely from one side of the alternating system to the other, acting as a sort of particle-in-a-box. The wavelengths of light absorbed by the molecules can be very well approximated by applying expressions derived for the particle-in-a-box system. Although it is not a perfect fit between theory and experiment, it is close enough that we acknowledge the usefulness of the particle-in-a-box model.

[†] Sometimes the expression $\Psi^*\Psi$ is written as $|\Psi|^2$, indicating that it is a real (that is, nonimaginary) value.

Example 10.13

β-Carotenes are highly conjugated polyenes found in many vegetables. They can be oxidized and used to synthesize pigments that play important roles in the chemistry of mammalian vision. The parent compound, β-carotene, has a maximum absorption of light that occurs at 480 nm. If this transition corresponds to an $n = 11$ to $n = 12$ transition of an electron in a particle-in-a-box system, what is the approximate length of the molecular "box"?

Solution

First, we should convert the wavelength of the light absorbed into the equivalent energy in joules:

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J·s})(2.9979 \times 10^{8}\ \text{m/s})}{4.8 \times 10^{-7}\ \text{m}} = 4.14 \times 10^{-19}\ \text{J}$$

Next, using this value for the change in energy for the transition and the expression for the particle-in-a-box energy values, we can set up the following relationship:

$$\begin{aligned}\Delta E &= E_{12} - E_{11}\\ &= \frac{12^2h^2}{8m_ea^2} - \frac{11^2h^2}{8m_ea^2} = (144 - 121)\frac{h^2}{8m_ea^2} = 23\frac{h^2}{8m_ea^2} = 4.14 \times 10^{-19}\ \text{J}\end{aligned}$$

In the last step, we are equating the energy difference between the two energy levels with the energy of the light absorbed. We know the value of h and m_e, so we can substitute and solve for a, the length of the molecular "box." We get

$$\frac{23 \cdot (6.626 \times 10^{-34}\ \text{J·s})^2}{8 \cdot (9.109 \times 10^{-31}\ \text{kg}) \cdot a^2} = 4.14 \times 10^{-19}\ \text{J}$$

$$a^2 = \frac{23 \cdot (6.626 \times 10^{-34}\ \text{J·s})^2}{8 \cdot (9.109 \times 10^{-31}\ \text{kg}) \cdot 4.14 \times 10^{-19}\ \text{J}}$$

All units cancel except for m^2 in the numerator. (You have to decompose the J unit to get this, however.) Evaluating:

$$a^2 = 3.35 \times 10^{-18}\ \text{m}^2$$

$$a = 1.83 \times 10^{-9}\ \text{m} = 18.3\ \text{Å}$$

Experimentally, we find that a β-carotene molecule has a length of about 29 Å—not perfect agreement, but still good enough to be used for qualitative purposes, especially in comparing similar molecules of different conjugation lengths.

10.10 Tunneling

We have assumed in the particle-in-a-box model that the potential energy outside the box is infinity, so that the particle has absolutely no chance of penetrating the wall. The wavefunction is identically zero at any position where the potential energy is infinity. Suppose the potential energy weren't infinity, just some very large value K? What if it weren't so large after all, just some value higher than the energy of the particle? If the wall were limited in width (that is, if some area on the other side had $V = 0$ again), how would that affect the wavefunction?

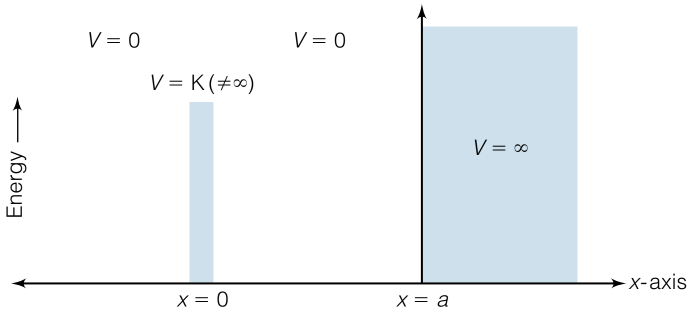


Figure 10.8 A potential energy diagram where tunneling can occur. Many real systems mimic this sort of potential energy scheme. Tunneling is an observable phenomenon that is not predicted by classical mechanics.

This system is illustrated in Figure 10.8, and actually describes a large number of physically real systems. For example, a very fine metal point can be brought very close—within several angstroms, but still not in physical contact—to a clean surface. The gap between the two pieces of matter represents a finite potential energy barrier whose height is higher in energy than the energy of the electrons on either side.

The acceptable wavefunctions of an electron on one side of the system *must* be determined by application of the postulates of quantum mechanics. In particular, the Schrödinger equation must be satisfied by any wavefunction that a particle can have. Inside the regions in Figure 10.8 where the potential energy is zero, the wavefunctions are similar to the particle-in-a-box. But for the region where the potential energy has a nonzero, noninfinite value,

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi + \hat{V}\Psi = E\Psi$$

must be solved. Assuming that the potential energy V is some constant independent of x but larger than E, this expression can be algebraically rearranged into

$$\frac{2m(V - E)}{\hbar^2}\Psi = \frac{\partial^2}{\partial x^2}\Psi$$

This second-order differential equation has a known analytic solution. The general wavefunctions that satisfy the above equation are

$$\Psi = Ae^{kx} + Be^{-kx} \tag{10.14}$$

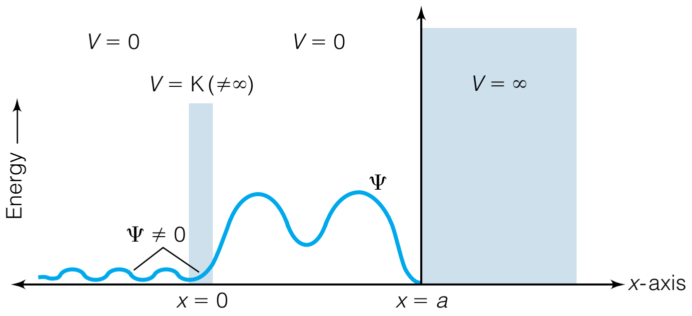
where

$$k = \left[\frac{2m(V - E)}{\hbar^2}\right]^{1/2}$$

Note the similarity of the wavefunction in equation 10.14 and the exponential form of the wavefunctions for the particle-in-a-box (shown in the first footnote in Section 10.8). In this case, however, the exponentials have real exponents, not imaginary exponents.

Without additional information about the system, we cannot say much about the exact form (in terms of A and B) of the wavefunctions in this region. For example, Ψ over the entire space must be continuous, and that places some restrictions on the values of A and B in terms of the length of the zero-potential region and the wavefunctions in that region. But there is one thing we can note immediately: the wavefunction is not zero in the region of Figure 10.8

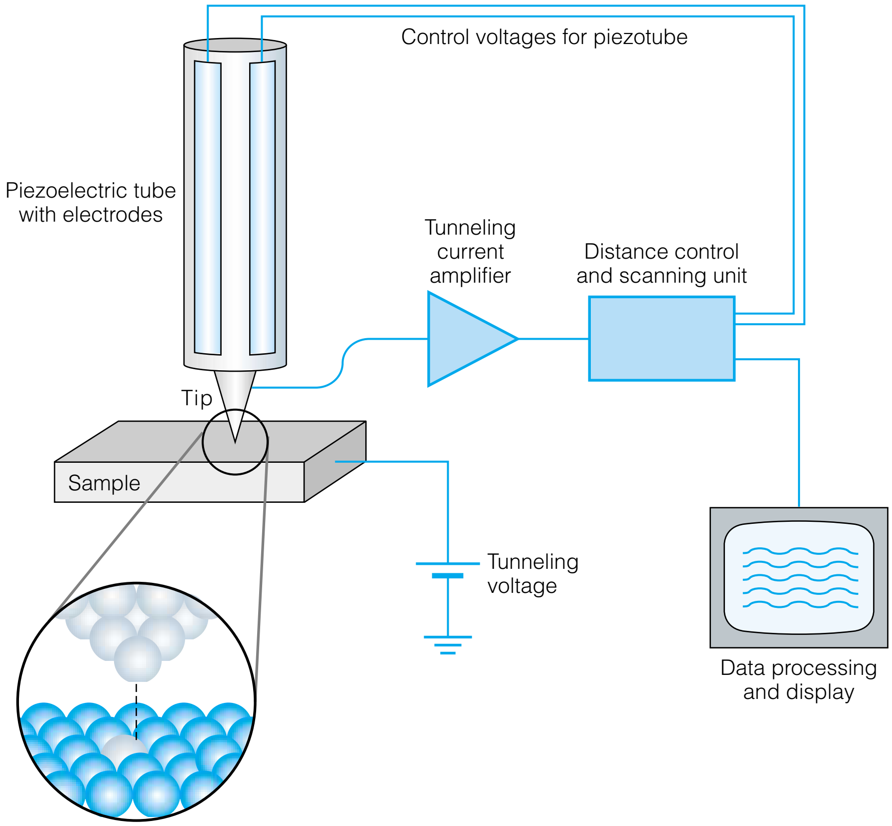
Figure 10.9 Due to the noninfinite height and depth of the potential energy barrier, the wavefunction has a nonzero probability of existing on the other side of the barrier. Alpha particle decay and small gaps between two surfaces are two systems where tunneling occurs.



where the potential energy is high, even if the potential energy is greater than the total energy of the particle. Furthermore, the mathematical form of this wavefunction guarantees that it will not equal zero for any finite value of x. This means that there is a nonzero probability that a particle with this wavefunction will exist at the other side of the box, even though the total energy of the particle is less than the potential barrier. This is illustrated qualitatively in Figure 10.9. Classically, if the barrier were higher than the total energy, the particle couldn't exist on the other side of the barrier. Quantum mechanically, it can. This is called *tunneling*.

Tunneling is a simple yet profound prediction of quantum mechanics. After these conclusions were announced, in 1928 Russian scientist George Gamow used tunneling as an explanation of alpha decay in radioactive nuclei. There had been speculation about exactly how the alpha particle (a helium nucleus) could escape the huge potential energy barrier of the other nuclear particles. More recently, we have seen the development of the scanning tunneling microscope (STM). This simple device, illustrated in Figure 10.10, uses tunneling

Figure 10.10 A commercial scanning tunneling microscope (STM). Invented in the early 1980s, STMs take advantage of a quantum-mechanical phenomenon.



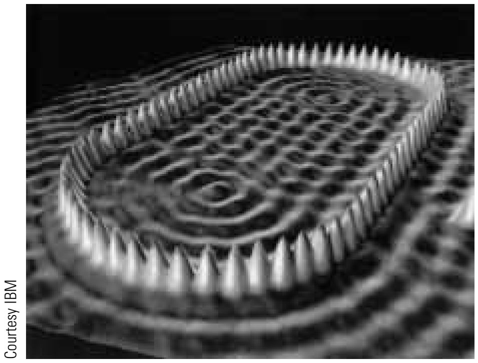


Figure 10.11 An STM image of a ring of Fe atoms on a copper surface.

of electrons to pass a very, very small gap between a sharp tip and a surface. Since the amount of tunneling varies exponentially with distance, even very small distance changes can yield very large differences in the amount of electron tunneling (measured as a current, since current is the flow of electrons). The extreme sensitivity of the STM allows one to make pictures of smooth surfaces *on an atomic scale*. Figure 10.11 shows an image measured by an STM.

Tunneling is a real, detectable phenomenon. It is not predicted by classical mechanics (and would be forbidden by it) but it arises naturally out of quantum mechanics. Its existence is the first real-life example given here of the strange and wonderful world of quantum theory.

10.11 The Three-Dimensional Particle-in-a-Box

The one-dimensional particle-in-a-box can be expanded to two and three dimensions very easily. Because the treatments are similar, we consider just the three-dimensional system here (and we trust that the student will be able to simplify the following treatment for a two-dimensional system; see exercise 10.53 at the end of this chapter). A general system, showing a box having its origin at (0, 0, 0) and having dimensions $a \times b \times c$, is illustrated in Figure 10.12. Once again we define the system with $V = 0$ inside the box and $V = \infty$ outside the box. The Schrödinger equation for a particle in a three-dimensional box is

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi = E\Psi \qquad \textbf{(10.15)}$$

The three-dimensional operator $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ is very common and is given the symbol ∇^2, called "del-squared" and referred to as the *Laplacian operator:*

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2} \qquad \textbf{(10.16)}$$

The 3-D Schrödinger equation is usually written as

$$\frac{-\hbar^2}{2m}\nabla^2\Psi = E\Psi$$

In the rest of this text, we use the symbol ∇^2 to represent the Laplacian for a particular system that operates on Ψ in the Schrödinger equation.

We determine the acceptable wavefunctions for this system by trying another assumption. Let us assume that the complete three-dimensional $\Psi(x, y, z)$, which must be a function of x, y, and z, can be written as a product of three functions, each of which can be written in terms of *only* one variable. That is:

$$\Psi(x, y, z) = X(x)\cdot Y(y)\cdot Z(z) \qquad \textbf{(10.17)}$$

where $X(x)$ is a function only of x (that is, independent of y and z), $Y(y)$ is a function solely of y, and $Z(z)$ is a function solely of z. Wavefunctions that can be written this way are said to be *separable*. Why make this particular assumption? Because then in the evaluation of the del-squared part of the Schrödinger equation, each second derivative will act on only one of the separate functions and the others will cancel, making an ultimate solution of the Schrödinger equation that much simpler.

We also simplify the notation by dropping the parenthetical variables on the three functions. The Schrödinger equation in equation 10.15 becomes

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)XYZ = E\cdot XYZ$$

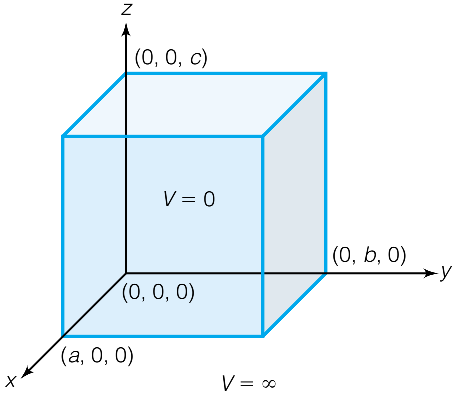


Figure 10.12 The three-dimensional particle-in-a-box. An understanding of its wavefunctions is based on the wavefunctions of the 1-D particle-in-a-box, and it illustrates the concept of separation of variables. Generally, $a \neq b \neq c$, although when $a = b = c$ the wavefunctions may have some special characteristics.

Now we distribute the product XYZ to all three derivatives in the Hamiltonian operator:

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}XYZ + \frac{\partial^2}{\partial y^2}XYZ + \frac{\partial^2}{\partial z^2}XYZ\right) = E \cdot XYZ$$

Next we take advantage of a property of partial derivatives: they act on the stated variable only and assume that any other variables are constant. In the first derivative term, the partial derivative is taken with respect to x, meaning that y and z are held constant. As we defined it above, only the X function depends on the variable x; the functions Y and Z do not. Thus, the entire function Y and the entire function Z—whatever they are—are constants and can be removed to outside the derivative. The first term then looks like this:

$$YZ \cdot \frac{d^2}{dx^2}X$$

The same analysis can be applied to the second and third derivatives, which deal with y and z, respectively. The Schrödinger equation can therefore be rewritten as

$$\frac{-\hbar^2}{2m}\left(YZ\frac{d^2}{dx^2}X + XZ\frac{d^2}{dy^2}Y + XY\frac{d^2}{dz^2}Z\right) = E \cdot XYZ$$

Finally, let us divide both sides of this expression by XYZ and bring $-\hbar^2/2m$ to the other side. Some of the functions will cancel from each term on the left side, leaving us with

$$\left(\frac{1}{X}\frac{d^2}{dx^2}X + \frac{1}{Y}\frac{d^2}{dy^2}Y + \frac{1}{Z}\frac{d^2}{dz^2}Z\right) = -\frac{2mE}{\hbar^2}$$

Each term on the left side depends on a single variable: either x, or y, or z. Every term on the right side is a constant: 2, m, E, and $\hbar$. In such a case, every term on the left side must also be a constant—this being the only way that the three terms, each dependent on a different variable, could sum up to a constant value. Let us define the first term as $-(2mE_x)/\hbar^2$:

$$\frac{1}{X}\frac{d^2}{dx^2}X \equiv -\frac{2mE_x}{\hbar^2}$$

where E_x is the energy of the particle that derives from the X part of the overall wavefunction. Similarly, for the second and third terms:

$$\frac{1}{Y}\frac{d^2}{dy^2}Y \equiv -\frac{2mE_y}{\hbar^2}$$

$$\frac{1}{Z}\frac{d^2}{dz^2}Z \equiv -\frac{2mE_z}{\hbar^2}$$

where E_y and E_z are the energies derived from the Y and Z parts of the overall wavefunction. These three expressions can be rewritten as

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}X &= E_xX \\ -\frac{\hbar^2}{2m}\frac{d^2}{dy^2}Y &= E_yY \qquad \textbf{(10.18)} \\ -\frac{\hbar^2}{2m}\frac{d^2}{dz^2}Z &= E_zZ \end{aligned}$$

In comparing these three equations with the original Schrödinger equation for this system, it is not too difficult to see that

$$E = E_x + E_y + E_z \tag{10.19}$$

We have seen expressions of the form given in equations 10.18: *they have the same form as the Schrödinger equation for the one-dimensional particle-in-a-box.* Rather than having to re-derive solutions for the three-dimensional case, we can simply use the same functions, but with the appropriate labels for a three-dimensional system. Therefore, the solution for the x dimension is

$$X(x) = \sqrt{\frac{2}{a}}\sin\frac{n_x\pi x}{a}$$

where n_x is 1, 2, 3, 4 . . . and is a quantum number (note the x subscript on the quantum number). The quantized energy, E_x, can also be taken from the one-dimensional box system:

$$E_x = \frac{n_x^2h^2}{8ma^2}$$

This analysis can be repeated for the other two dimensions. It should be readily apparent that the answers are similar:

$$Y(y) = \sqrt{\frac{2}{b}}\sin\frac{n_y\pi y}{b}$$

$$Z(z) = \sqrt{\frac{2}{c}}\sin\frac{n_z\pi z}{c}$$

Y and Z depend only on the coordinates y and z respectively. The constants b and c represent the lengths of the box in the y and z direction, and the quantum numbers n_y and n_z refer to the corresponding dimension only. Remember, however, that the wavefunction Ψ is the product of X, Y, and Z, so that the complete 3-D wavefunction is

$$\Psi(x, y, z) = \sqrt{\frac{8}{abc}}\sin\frac{n_x\pi x}{a}\cdot\sin\frac{n_y\pi y}{b}\cdot\sin\frac{n_z\pi z}{c} \tag{10.20}$$

where the constants have all been grouped together. The total energy for a particle in this three-dimensional box is

$$E = \frac{n_x^2h^2}{8ma^2} + \frac{{n_y}^2h^2}{8mb^2} + \frac{{n_z}^2h^2}{8mc^2} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \tag{10.21}$$

Although the wavefunctions of the 3-D particle-in-a-box are qualitatively similar to those for the 1-D particle-in-a-box, there are some differences. First, every observable has three parts: an x part, a y part, and a z part. (See the expression for E in equation 10.21.) For example, the momentum of a particle in a 3-D box is more properly referred to as a momentum in the x direction, denoted p_x; a momentum in the y direction, p_y; and a momentum in the z direction, p_z. Each observable has a corresponding operator, which in the momentum example is either $\widehat{p_x}$, $\widehat{p_y}$, or $\widehat{p_z}$:

$$\begin{aligned} \widehat{p_x} &= -i\hbar\frac{\partial}{\partial x} \\ \widehat{p_y} &= -i\hbar\frac{\partial}{\partial y} \\ \widehat{p_z} &= -i\hbar\frac{\partial}{\partial z} \end{aligned} \tag{10.22}$$

Despite the separated wavefunctions in one dimension each, it is important to understand that the operator must operate on the entire wavefunction. Although the entire wavefunction is in three dimensions, the one-dimensional operator acts only on the part that depends on the coordinate of interest.

Also, it needs to be understood that average values are treated differently in the 3-D case than in the 1-D case, because of the additional dimensions. Because each dimension is independent of the other, an integration must be performed over each dimension independently. This triples the number of integrals to be evaluated, but since the wavefunction can be separated into x, y, and z parts, the integrals are straightforward to evaluate. Since this system is three-dimensional, the $d\tau$ for the integration must have three infinitesimals: $d\tau = dx\,dy\,dz$. For normalized wavefunctions, the average value of an observable is thus given by

$$\langle A\rangle = \int_x\int_y\int_z \Psi^*\widehat{A}\Psi\,dx\,dy\,dz \tag{10.23}$$

For wavefunctions and operators that are separable into x, y, and z parts, this triple integral ultimately separates into the product of three integrals:

$$\langle A\rangle = \int_x \Psi_x^*\widehat{A_x}\Psi_x\,dx\cdot\int_y \Psi_y^*\widehat{A_y}\Psi_y\,dy\cdot\int_z \Psi_z^*\widehat{A_z}\Psi_z\,dz$$

Each integral has its own limits, depending on the limits of the particular system in that dimension. If the operator does not include a certain dimension, then it has no influence on the integral over that dimension. The following example illustrates.

Example 10.14

Although the particle-in-a-box wavefunctions are not eigenfunctions of the momentum operators, we can determine average or expectation values for the momentum. Find $\langle p_y\rangle$ for the 3-D wavefunction

$$\Psi(x, y, z) = \sqrt{\frac{8}{abc}}\sin\frac{1\pi x}{a}\cdot\sin\frac{2\pi y}{b}\cdot\sin\frac{3\pi z}{c}$$

(This wavefunction has $n_x = 1$, $n_y = 2$, and $n_z = 3$.)

Solution

In order to determine $\langle p_y\rangle$, the following integral must be evaluated:

$$\langle p_y\rangle = \int_x\int_y\int_z \sqrt{\frac{8}{abc}}\sin\frac{1\pi x}{a}\cdot\sin\frac{2\pi y}{b}\cdot\sin\frac{3\pi z}{c}$$
$$\times -i\hbar\frac{\partial}{\partial y}\left(\sqrt{\frac{8}{abc}}\sin\frac{1\pi x}{a}\cdot\sin\frac{2\pi y}{b}\cdot\sin\frac{3\pi z}{c}\right)dx\,dy\,dz$$

Although this looks complicated, it can be simplified into the product of three integrals, where the normalization constant will be split appropriately and the operator, affecting only the y part of Ψ, appears only in the integral over y:

$$\langle p_y\rangle = \int_{x=0}^{a}\sqrt{\frac{2}{a}}\sin\frac{1\pi x}{a}\sqrt{\frac{2}{a}}\sin\frac{1\pi x}{a}\,dx$$
$$\times\int_{y=0}^{b}\sqrt{\frac{2}{b}}\sin\frac{2\pi y}{b}\cdot -i\hbar\frac{\partial}{\partial y}\sqrt{\frac{2}{a}}\sin\frac{2\pi y}{b}\,dy$$
$$\times\int_{z=0}^{c}\sqrt{\frac{2}{c}}\sin\frac{3\pi z}{c}\sqrt{\frac{2}{c}}\sin\frac{3\pi z}{c}\,dz$$

This product of three integrals is relatively easy to evaluate, despite its length. The x and z integrals are exactly the same as the one-dimensional particle-in-a-box wavefunctions being evaluated from one end of the box to the other, *and they are normalized*. Therefore the first and the third integrals are each 1. The expression becomes

$$\langle p_y\rangle = 1 \cdot \int\limits_{y=0}^{b} \sqrt{\frac{2}{b}} \sin\frac{2\pi y}{b} \cdot -i\hbar\frac{\partial}{\partial y}\sqrt{\frac{2}{a}} \sin\frac{2\pi y}{b}\, dy \cdot 1$$

For the y part, evaluation of the derivative part of the operator is straightforward, and rewriting the integral, bringing all constants outside the integral sign, yields

$$\langle p_y\rangle = \frac{2}{b} \cdot \frac{2\pi}{b} \cdot -i\hbar \int\limits_{y=0}^{b} \sin\frac{2\pi y}{b} \cdot \cos\frac{2\pi y}{b}\, dy$$

Using the integral table in Appendix 1, we find that this integral is exactly zero. Therefore,

$$\langle p_y\rangle = 0$$

This should not be too much of a surprise. Although the particle certainly has momentum at any given moment, it will have one of two opposite momentum vectors exactly half the time. Because the opposing momentum vectors cancel each other out, the *average value* of the momentum is zero.

The above example illustrates that although the triple integral may look difficult, it separates into more manageable parts. This separability of the integral is directly related to our assumption that the wavefunction itself is separable. Without separability of Ψ, we would have to solve a triple integral in three variables simultaneously—a formidable task! We will see other examples of how separability of Ψ makes things easier for us. Ultimately, the issue of separability is paramount in the application of the Schrödinger equation to real systems.

10.12 Degeneracy

For the one-dimensional particle-in-a-box, all of the energies of the eigenfunctions are different. For the general 3-D particle-in-a-box, because the total energy depends on not only the quantum numbers n_x, n_y, and n_z but also the individual dimensions of the box a, b, and c, one can imagine that in some cases the quantum numbers and the lengths might be such that different sets of quantum numbers $\{n_x, n_y, n_z\}$ would yield the *same* energy for the two *different* wavefunctions.

This situation is very possible in systems that are symmetric. Consider a cubical box: $a = b = c$. Using the variable a to stand for any side of the cubical box, the wavefunctions and energies now become

$$\Psi(x, y, z) = \sqrt{\frac{8}{a^3}} \sin\frac{n_x\pi x}{a} \cdot \sin\frac{n_y\pi y}{a} \cdot \sin\frac{n_z\pi z}{a} \tag{10.24}$$

$$E = \frac{n_x^2h^2}{8ma^2} + \frac{n_y^2h^2}{8ma^2} + \frac{n_z^2h^2}{8ma^2} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \tag{10.25}$$

The energy depends on a set of constants and the sum of the squares of the quantum numbers. If a set of three quantum numbers adds up to the same total as another set of three different quantum numbers, or if the quantum numbers themselves exchange values, the energies would be exactly the same even though the wavefunctions are different. This condition is called *degeneracy.* Different, linearly independent wavefunctions that have the same energy are called *degenerate.* A specific level of degeneracy is indicated by the number of different wavefunctions that have the exact same energy. If there are two, the energy level is called *twofold* (or *doubly*) degenerate; if there are three wavefunctions, it is *threefold* (or *triply*) degenerate; and so on.

From equation 10.25, the specific energy is determined by what values the quantum numbers have. We can label each energy as E_{xyz} where the x, y, and z labels indicate what the appropriate quantum numbers are. Thus,

$$E_{111} = \frac{h^2}{8ma^2}(1 + 1 + 1) = 3 \cdot \frac{h^2}{8ma^2}$$

$$E_{112} = \frac{h^2}{8ma^2}(1 + 1 + 4) = 6 \cdot \frac{h^2}{8ma^2}$$

$$E_{113} = \frac{h^2}{8ma^2}(1 + 1 + 9) = 11 \cdot \frac{h^2}{8ma^2}$$

and so forth. (It is easier to illustrate this point by leaving the energies in terms of h, m, and a instead of evaluating their exact values in terms of joules.) E_{112} is the eigenvalue of the wavefunction that has $n_x = 1$, $n_y = 1$, and $n_z = 2$. We also have the following two wavefunctions:

$$\Psi_{121} = \sqrt{\frac{8}{a^3}} \sin \frac{1\pi x}{a} \cdot \sin \frac{2\pi y}{a} \cdot \sin \frac{1\pi z}{a}$$

$$\Psi_{211} = \sqrt{\frac{8}{a^3}} \sin \frac{2\pi x}{a} \cdot \sin \frac{1\pi y}{a} \cdot \sin \frac{1\pi z}{a}$$

where we are now starting to label the wavefunctions as Ψ_{xyz}, like the energies. These are *different* wavefunctions. You should satisfy yourself that they are different. (One has the quantum number 2 in the x dimension and the other has the quantum number 2 in the y dimension.) Their energies are

$$E_{121} = \frac{h^2}{8ma^2}(1 + 4 + 1) = 6 \cdot \frac{h^2}{8ma^2}$$

$$E_{211} = \frac{h^2}{8ma^2}(4 + 1 + 1) = 6 \cdot \frac{h^2}{8ma^2}$$

E_{121} and E_{211} are the same as E_{112}, even though each energy observable corresponds to a different wavefunction. This value of energy is threefold degenerate. There are three *different* wavefunctions that have the same energy. (Degenerate wavefunctions may have different eigenvalues of other observables.)

This example of degeneracy is a consequence of a wavefunction in three-dimensional space where each dimension is independent but equivalent. This might be considered *degeneracy by symmetry.* One can also find examples of *accidental* degeneracy. For example, a cubical box has wavefunctions with the sets of quantum numbers (3, 3, 3) and (5, 1, 1), and the energies are

$$E_{333} = \frac{h^2}{8ma^2}(9 + 9 + 9) = 27 \cdot \frac{h^2}{8ma^2}$$

$$E_{511} = \frac{h^2}{8ma^2}(25 + 1 + 1) = 27 \cdot \frac{h^2}{8ma^2}$$

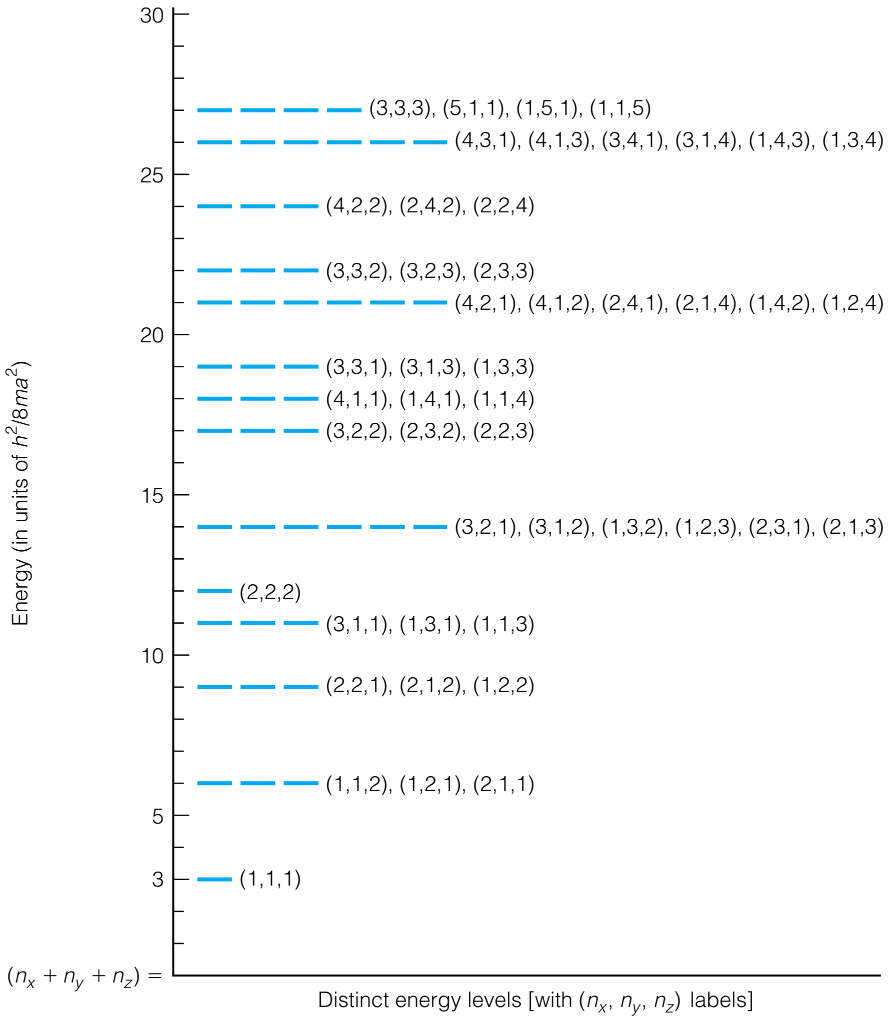


Figure 10.13 The energy levels of the 3-D particle-in-a-(cubical)-box. In this system, different wavefunctions can have the same energy. This is an example of degeneracy.

Here is an example of degeneracy by accident. The corresponding wavefunctions have no common quantum numbers, but their energy eigenvalues are exactly the same. If we recognize that E_{151} and E_{115} also have the same energy, the level of degeneracy in this example becomes *fourfold.* A diagram of the energy levels of the 3-D particle-in-a-box is shown in Figure 10.13 and illustrates the degeneracies of the energy levels.

Example 10.15

Write the four wavefunctions of a cubical box that have energy of $27(h^2/8ma^2)$ to show that they are indeed different eigenfunctions.

Solution

Using the combinations of quantum numbers (3, 3, 3), (5, 1, 1), (1, 5, 1), and (1, 1, 5) in the 3-D particle-in-a-box wavefunction:

$$\Psi_{333} = \sqrt{\frac{8}{a^3}} \sin \frac{3\pi x}{a} \cdot \sin \frac{3\pi y}{a} \cdot \sin \frac{3\pi z}{a}$$

$$\Psi_{511} = \sqrt{\frac{8}{a^3}} \sin\frac{5\pi x}{a} \cdot \sin\frac{1\pi y}{a} \cdot \sin\frac{1\pi z}{a}$$

$$\Psi_{151} = \sqrt{\frac{8}{a^3}} \sin\frac{1\pi x}{a} \cdot \sin\frac{5\pi y}{a} \cdot \sin\frac{1\pi z}{a}$$

$$\Psi_{115} = \sqrt{\frac{8}{a^3}} \sin\frac{1\pi x}{a} \cdot \sin\frac{1\pi y}{a} \cdot \sin\frac{5\pi z}{a}$$

(Here we are writing the quantum number 1 to illustrate the point; typically, 1 values aren't written explicitly.) It should be obvious that these four wavefunctions are all different, having integer quantum numbers that are either different or in different parts of the wavefunction.

10.13 Orthogonality

One other major property of wavefunctions needs to be introduced. We should recognize by now that a system has not just a single wavefunction but many possible wavefunctions, each of which has an energy (obtained using an eigenvalue equation) and perhaps other eigenvalue observables. We can summarize the multiple solutions to the Schrödinger equation by writing it as

$$\hat{H}\Psi_n = E_n\Psi_n \qquad n = 1, 2, 3, \ldots \tag{10.26}$$

Equation 10.26, when satisfied, usually yields not just a single wavefunction but a set of them (perhaps even an infinite number), like those for the particle-in-a-box. Mathematically, this set of equations has a very useful property. The wavefunctions must be normalized, for every Ψ_n:

$$\int_{\substack{\text{all}\\\text{space}}} \Psi_n^*\Psi_n \, d\tau = 1$$

This is the expression that defines normalization. If, on the other hand, two *different* wavefunctions were used in the above expression, the different wavefunctions Ψ_m and Ψ_n have a property *that requires that the integral be exactly zero*:

$$\int_{\substack{\text{all}\\\text{space}}} \Psi_m^*\Psi_n \, d\tau = 0 \qquad \Psi_m \neq \Psi_n \tag{10.27}$$

It does not matter in what order the wavefunctions are multiplied together. The integral will still be identically zero. This property is called *orthogonality;* the wavefunctions are *orthogonal* to each other. Orthogonality is useful because, once we know that all wavefunctions of a system are orthogonal to each other, many integrals become identically zero. We need only recognize that the wavefunctions inside an integral are different and we can apply the orthogonality property: that integral equals zero. Both wavefunctions must be for the same system, they must have different eigenvalues,[†] and there must be no operator in the integral sign (there may be a constant operator, but constants can be removed from inside the integral and what remains must satisfy equation 10.27).

[†] Equation 10.26 does not apply if the two wavefunctions Ψ_m and Ψ_n have the same energy eigenvalue (that is, if they are degenerate). Other considerations are necessary to circumvent this, but we will not discuss that here.

The orthogonality and normality properties of wavefunctions are usually combined into a single expression termed *orthonormality:*

$$\int \Psi_m^* \Psi_n \, d\tau = \begin{cases} 0 \text{ if } m \neq n \\ 1 \text{ if } m = n \end{cases} \tag{10.28}$$

Example 10.16

Demonstrate explicitly that for the 1-D particle-in-a-box, Ψ_1 is orthogonal to Ψ_2.

Solution

Evaluate the following integral:

$$\frac{2}{a}\int_0^a \sin\frac{1\pi x}{a}\sin\frac{2\pi x}{a}\,dx$$

(The $2/a$ constant has been pulled outside the integral, and the limits of integration are properly set as 0 to a.) Using the integral table in Appendix 1:

$$\begin{aligned}\frac{2}{a}\int_0^a \sin\frac{1\pi x}{a}\sin\frac{2\pi x}{a}\,dx &= \frac{2}{a}\cdot\left[\frac{\sin\left(\frac{1\pi}{a}-\frac{2\pi}{a}\right)x}{2\left(\frac{1\pi}{a}-\frac{2\pi}{a}\right)} - \frac{\sin\left(\frac{1\pi}{a}+\frac{2\pi}{a}\right)x}{2\left(\frac{1\pi}{a}+\frac{2\pi}{a}\right)}\right]\Bigg|_0^a \\ &= \frac{2}{a}\cdot\left[\frac{\sin\left(-\frac{1\pi}{a}\right)x}{\left(-\frac{2\pi}{a}\right)} - \frac{\sin\left(\frac{3\pi}{a}\right)x}{\left(\frac{6\pi}{a}\right)}\right]\Bigg|_0^a\end{aligned}$$

Substituting the limits 0 and a into this expression and evaluating:

$$= \frac{2}{a}\cdot\left[\frac{\sin\left(-\frac{1\pi}{a}\right)\cdot a}{\left(-\frac{2\pi}{a}\right)} - \frac{\sin\left(\frac{3\pi}{a}\right)\cdot a}{\left(\frac{6\pi}{a}\right)}\right] - \frac{2}{a}\cdot\left[\frac{\sin\left(-\frac{1\pi}{a}\right)\cdot 0}{\left(-\frac{2\pi}{a}\right)} - \frac{\sin\left(\frac{3\pi}{a}\right)\cdot 0}{\left(\frac{6\pi}{a}\right)}\right]$$

$$= \frac{2}{a}\cdot\left[\frac{\sin(-\pi)}{\left(-\frac{2\pi}{a}\right)} - \frac{\sin(3\pi)}{\left(\frac{6\pi}{a}\right)}\right] - \frac{2}{a}\cdot\left[\frac{\sin 0}{\left(-\frac{2\pi}{a}\right)} - \frac{\sin 0}{\left(\frac{6\pi}{a}\right)}\right]$$

$$= \frac{2}{a}\cdot\left[\frac{0}{\left(-\frac{2\pi}{a}\right)} - \frac{0}{\left(\frac{6\pi}{a}\right)}\right] - \frac{2}{a}\cdot\left[\frac{0}{\left(-\frac{2\pi}{a}\right)} - \frac{0}{\left(\frac{6\pi}{a}\right)}\right] = 0$$

Therefore,

$$\frac{2}{a}\int_0^a \sin\frac{1\pi x}{a}\sin\frac{2\pi x}{a}\,dx = 0$$

which is exactly as it should be for orthogonal functions. You should satisfy yourself that you get the same answer if you evaluate the integral when you take the complex conjugate of Ψ_2 instead of Ψ_1.

Orthonormality is a very useful concept. Integrals whose values are exactly 0 or exactly 1 make mathematical derivations much easier, and it is important that you develop the skill to recognize when integrals are exactly 1 (because the wavefunctions in the integrand are normalized) or exactly 0 (because the wavefunctions in the integrand are orthogonal). Finally, note that the orthonormality condition requires that *no operator be present inside the integral.* If an operator is present, the operation must be evaluated before you can consider whether the integral can be exactly 0 or 1.

10.14 The Time-Dependent Schrödinger Equation

Although the time-independent Schrödinger equation is heavily utilized in this chapter, it is not the fundamental form of the Schrödinger equation. Only stationary states—wavefunctions whose probability distributions do not vary over time—provide meaningful eigenvalues using the time-independent Schrödinger equation. There is a form of the Schrödinger equation that does include time. It is called the *time-dependent Schrödinger equation*, and has the form

$$\widehat{H}\Psi(x, t) = i\hbar\frac{\partial\Psi(x, t)}{\partial t} \tag{10.29}$$

where the x- and t-dependence on Ψ are written explicitly to indicate that Ψ does vary with time as well as position. Schrödinger postulated that all wavefunctions must satisfy this differential equation, and it is the last postulate we will consider, if only briefly. This postulate is what establishes the prime importance of the Hamiltonian operator in quantum mechanics.

One common way to approach equation 10.29 is to assume the separability of time and position, similar to our separation of x, y, and z in the 3-D box. That is,

$$\Psi(x, t) = f(t) \cdot \Psi(x) \tag{10.30}$$

where part of the complete wavefunction depends only on time and part depends only on position. Although it is fairly straightforward to derive, we will omit the derivation and simply present the following statement of acceptable solutions of $\Psi(x, t)$:

$$\Psi(x, t) = e^{-iEt/\hbar} \cdot \Psi(x) \tag{10.31}$$

where E is the total energy of the system. This solution for the time-dependence of a wavefunction places no restriction on the form of the position-dependent function $\Psi(x)$. With respect to wavefunctions, we are right back where we started at the beginning of the chapter. With this assumption, the time-dependence of the total wavefunction is rather simple in form, and the position dependence of the total wavefunction needs to be considered for the system of interest. If t can be separated from position in $\Psi(x, t)$ and the wavefunction has the form from equation 10.31, then the time-dependent Schrödinger equation simplifies into the time-independent Schrödinger equation, as shown below.

Example 10.17

Show that solutions for Ψ given in equation 10.31, when used in the time-dependent Schrödinger equation, yield the time-independent Schrödinger equation.

Solution

Using the separated solution for $\Psi(x, t)$:

$$\widehat{H}[e^{-iEt/\hbar} \cdot \Psi(x)] = i\hbar\frac{\partial}{\partial t}[e^{-iEt/\hbar} \cdot \Psi(x)]$$

Taking the derivative of the exponential with respect to time [the derivative does not affect $\Psi(x)$, since it doesn't depend on time]:

$$\widehat{H}[e^{-iEt/\hbar} \cdot \Psi(x)] = i\hbar \cdot \Psi(x) \cdot \frac{-iE}{\hbar} \cdot [e^{-iEt/\hbar}]$$

On the right, $\hbar$ cancels, and the minus sign cancels i^2. Since the Hamiltonian operator does not include time, the exponential on the left side can be removed to outside the operator. Then we have:

$$e^{-iEt/\hbar} \cdot \widehat{H}\Psi(x) = E \cdot \Psi(x) \cdot e^{-iEt/\hbar}$$

The exponentials on both sides cancel each other, and what is left is

$$\widehat{H}\Psi(x) = E\Psi(x)$$

which is the time-independent Schrödinger equation.

The above example shows how the time-dependent Schrödinger equation produces the time-independent Schrödinger equation, assuming a certain form of $\Psi(x, t)$ and a time-independent $\widehat{H}$. It is therefore more correct to say that equation 10.29 is the fundamental equation of quantum mechanics, but given the separability assumption, more attention in textbooks is devoted to understanding the position-dependent part of the complete, time-dependent Schrödinger equation. It is easy to show that wavefunctions of the form in equation 10.31 are stationary states, because their probability distributions do not depend on time. Some wavefunctions are not of the form in equation 10.31, so the time-dependent Schrödinger equation must be used.

10.15 Summary

Table 10.2 lists the postulates of quantum mechanics (even those not specifically discussed in this chapter). Different sources list different numbers of postulates, some broken into independent statements and some grouped together. Hopefully, you can see how we applied these statements to the first ideal system, the particle-in-a-box.

Table 10.2 The postulates of quantum mechanics

Postulate I. The state of a system of particles is given by a wavefunction Ψ, which is a function of the coordinates of the particles and the time. Ψ contains all information that can be determined about the state of the system. Ψ must be single-valued, continuous, and bounded, and $|\Psi|^2$ must be integrable. (Discussed in section **10.2**)

Postulate II. For every physical observable or variable O, there exists a corresponding Hermitian operator $\widehat{O}$. Operators are constructed by writing their classical expressions in terms of position and (linear) momentum, then replacing "x times" (that is, $x\,\cdot$) for each x variable and $-i\hbar(\partial/\partial x)$ for each p_x variable in the expression. Similar substitutions must be made for y and z coordinates and momenta. (Section **10.3**)

Postulate III. The only values of observables that can be obtained in a single measurement are the eigenvalues of the eigenvalue equation constructed from the corresponding operator and the wavefunction Ψ:

$$\widehat{O}\Psi = K \cdot \Psi$$

where K is a constant. (Section **10.3**)

Postulate IV. Wavefunctions must satisfy the time-dependent Schrödinger equation:

$$\widehat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

(Section **10.14**) (If it is assumed that Ψ is separable into functions of time and position, we find that this expression can be rewritten to get the time-independent Schrödinger equation, $\widehat{H}\Psi = E\Psi$.) (section **10.7**)

Postulate V. The average value of an observable, $\langle O\rangle$, is given by the expression

$$\langle O\rangle = \int_{\substack{\text{all}\\\text{space}}} \Psi^*\widehat{O}\Psi\, d\tau$$

for normalized wavefunctions. (Section **10.9**)

Postulate VI. The set of eigenfunctions for any quantum mechanical operator is a complete mathematical set of functions.

Postulate VII. If, for a given system, the wavefunction Ψ is a linear combination of nondegenerate wavefunctions Ψ_n which have eigenvalues a_n:

$$\Psi = \sum_n c_n\Psi_n \quad \text{and} \quad \hat{A}\Psi_n = a_n\Psi_n$$

then the probability that a_n will be the value of the corresponding measurement is $|c_n|^2$. The construction of Ψ as the combination of all possible Ψ_n's is called the *superposition principle.*

Although no particle truly exists in a box having infinite walls, the particle-in-a-box illustrates all of the important aspects of quantum mechanics: satisfying the Schrödinger equation, normalization, orthogonality, quantized energy values, degeneracy. All other systems, real and ideal, also have these properties. We will continue the application of quantum mechanics to other ideal and real systems in the next chapter, where we will assume that the reader is familiar with these topics. If you are not, review the material in this chapter. It contains all of the preliminary background necessary to apply the quantum mechanical theory of atoms and molecules to any system, from the ideal particle-in-a-box to a DNA molecule. Although some new concepts will be presented in the following chapters, most of the basic components of quantum mechanics have already been covered. Any discussion of quantum mechanics is fundamentally based on the material in this chapter.

EXERCISES FOR CHAPTER 10

10.1. State the postulates of quantum mechanics introduced throughout the chapter in your own words.

10.2 Wavefunctions

10.2. What are four requirements for any acceptable wavefunction?

10.3. State whether the following functions are acceptable wavefunctions over the range given. If they are not, explain why not.

(a) $F(x) = x^2 + 1,\ 0 \le x \le 10$

(b) $F(x) = \sqrt{x} + 1,\ -\infty < x < +\infty$

(c) $f(x) = \tan(x),\ -\pi \le x \le \pi$

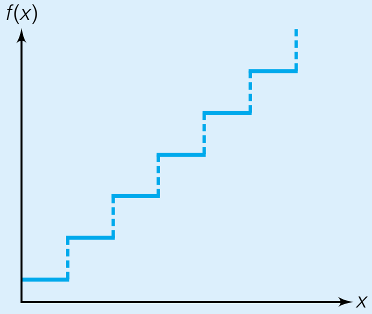
(d) $\Psi = e^{-x^2},\ -\infty < x < +\infty$

(e) $\Psi = e^{x^2},\ -\infty < x < +\infty$

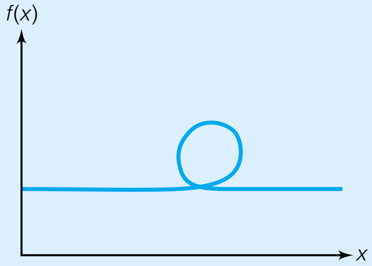
(f) $F(x) = \sin 4x,\ -\pi \le x \le +\pi$

(g) $x = y^2,\ x \ge 0$

(h) The function that looks like this:



(i) The function that looks like this:



10.3 Observables and Operators

10.4. What are the operations in the following expressions?

(a) 2×3

(b) $4 + 5$

(c) $\ln x^2$

(d) $\sin(3x - 3)$

(e) $e^{-\Delta E/kT}$

(f) $\frac{d}{dx}\left(4x^3 - 7x + \frac{7}{x}\right)$

10.5. Evaluate the operations in parts a, b, and f in the previous problem.

10.6. The following operators and functions are defined:

$$\hat{A} = \frac{\partial}{\partial x}(\ ) \qquad \hat{B} = \sin(\ ) \qquad \hat{C} = \frac{1}{(\ )} \qquad \hat{D} = 10^{(\ )}$$

$$p = 4x^3 - 2x^{-2} \qquad q = -0.5 \qquad r = 45xy^2 \qquad s = \frac{2\pi x}{3}$$

Evaluate: **(a)** $\hat{A}p$ **(b)** $\hat{C}q$ **(c)** $\hat{B}s$ **(d)** $\hat{D}q$ **(e)** $\hat{A}(\hat{C}r)$ **(f)** $\hat{A}(\hat{D}q)$

10.7. Multiple operators can act on a function. If $\widehat{P_x}$ acts on the coordinate x to yield $-x$, $\widehat{P_y}$ acts on the coordinate y to yield $-y$, and $\widehat{P_z}$ acts on the coordinate z to yield $-z$, evaluate the following expressions written in terms of 3-D Cartesian coordinates:

(a) $\widehat{P_x}(4, 5, 6)$ **(b)** $\widehat{P_y}\widehat{P_z}(0, -4, -1)$

(c) $\widehat{P_x}\widehat{P_x}(5, 0, 0)$ **(d)** $\widehat{P_y}\widehat{P_x}(\pi, \pi/2, 0)$

(e) Does $\widehat{P_x}\widehat{P_y}$ equal $\widehat{P_y}\widehat{P_x}$ for any set of coordinates? Why or why not?

10.8. Indicate which of the following expressions yield eigenvalue equations, and indicate the eigenvalue.

(a) $\frac{d}{dx}\sin\frac{\pi x}{2}$ **(b)** $\frac{d^2}{dx^2}\sin\frac{\pi x}{2}$

(c) $-i\hbar\frac{\partial}{\partial x}\sin\frac{\pi x}{2}$ **(d)** $-i\hbar\frac{\partial}{\partial x}e^{imx}$, where m is a constant

(e) $\frac{\partial}{\partial x}(e-x^2)$ **(f)** $\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + 0.5\right)\sin\frac{2\pi x}{3}$

10.9. Why is multiplying a function by a constant considered an eigenvalue equation?

10.10. Relating to the question above, some texts consider multiplying a function by zero to be an eigenvalue equation. Why might this be considered a problematic definition?

10.11. Using the original definition of the momentum operator and the classical form of kinetic energy, derive the one-dimensional kinetic energy operator

$$\hat{K} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$$

10.12. Under what conditions would the operator described as multiplication by i (the square root of -1) be considered a Hermitian operator?

10.13. A particle on a ring has a wavefunction

$$\Psi = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$

where ϕ equals 0 to 2π and m is a constant. Evaluate the angular momentum p_ϕ of the particle if

$$\widehat{p_\phi} = -i\hbar\frac{\partial}{\partial\phi}$$

How does the angular momentum depend on the constant m?

10.4 Uncertainty Principle

10.14. Calculate the uncertainty in position, Δx, of a baseball having mass 250 g going at 160 ± 2 km/hr. Calculate the uncertainty in position for an electron going at the same speed.

10.15. For an atom of mercury, an electron in the 1*s* shell has a velocity of about 58% (0.58) of the speed of light. At such speeds, relativistic corrections to the behavior of the electron are necessary. If the mass of the electron at such speeds is 1.23 m_e (where m_e is the rest mass of the electron) and the uncertainty in velocity is 10,000 m/s, what is the uncertainty in position of this electron?

10.16. How is the Bohr theory of the hydrogen atom inconsistent with the uncertainty principle? (In fact, it was this inconsistency, along with the theory's limited application to non-hydrogen-like systems, that limited Bohr's theory.)

10.17. Though not strictly equivalent, there is a similar uncertainty relationship between the observables time and energy:

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}$$

In emission spectroscopy, the width of lines (which gives a measure of ΔE) in a spectrum can be related to the lifetime (that is, Δt) of the excited state. If the width of a spectral line of a certain electronic transition is 1.00 cm^{-1}, what is the minimum uncertainty in the lifetime of the transition? Watch your units.

10.5 Probabilities

10.18. For a particle in a state having the normalized wavefunction

$$\Psi = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a}$$

in the range $x = 0$ to a, what is the probability that the particle exists in the following intervals?

(a) $x = 0$ to $0.02\ a$

(b) $x = 0.24a$ to $0.26a$

(c) $x = 0.49a$ to $0.51a$

(d) $x = 0.74a$ to $0.76a$

(e) $x = 0.98a$ to $1.00a$?

Plot the probabilities versus *x*. What does your plot illustrate about the probability?

10.19. A particle on a ring has a wavefunction $\Psi = e^{im\phi}$, where $\phi = 0$ to 2π and *m* is a constant.

(a) Normalize the wavefunction, where $d\tau$ is $d\phi$. How does the normalization constant depend on the constant *m*?

(b) What is the probability that the particle is in the ring indicated by the angular range $\phi = 0$ to $2\pi/3$? Does this answer make sense? How does the probability depend on the constant *m*?

10.20. A particle having mass *m* is described as having the (unnormalized) wavefunction $\Psi = k$, where *k* is some constant, when confined to an interval in one dimension, that interval having length *a* (that is, the interval of interest is $x = 0$ to *a*). What is the probability that the particle will exist in the first third of the interval, that is, from $x = 0$ to $(1/3)a$? What is the probability that the particle will be in the third third of the box, that is, from $x = (2/3)a$ to *a*?

10.21. Consider the same particle in the same box as in the previous problem, but the (unnormalized) wavefunction is different. Now, assume $\Psi = kx$, where the value of the wavefunction is directly proportional to the distance across the box. Evaluate the same two probabilities, and comment on the differences between the probabilities in this case and the previous one.

10.6 Normalization

10.22. What are the complex conjugates of the following wavefunctions? **(a)** $\Psi = 4x^3$ **(b)** $\Psi(\theta) = e^{i\pi\theta}$ **(c)** $\Psi = 4 + 3i$ **(d)** $\Psi = i \sin \frac{3\pi x}{2}$ **(e)** $\Psi = e^{-iEt/\hbar}$

10.23. Normalize the following wavefunctions over the range indicated. You may have to use the integral table in Appendix 1.

(a) $\Psi = x^2$, $x = 0$ to 1

(b) $\Psi = 1/x$, $x = 5$ to 6

(c) $\Psi = \cos x$, $x = -\pi/2$ to $\pi/2$

(d) $\Psi = e^{-r/a}$, $r = 0$ to ∞, *a* is a constant, $d\tau = 4\pi r^2\, dr$

(e) $\Psi = e^{-r^2/a}$, $r = -\infty$ to ∞, *a* is a constant. Use $d\tau$ from part d.

10.24. For an unbound (or "free") particle having mass *m* in the complete absence of any potential energy (that is, $V = 0$), the acceptable one-dimensional wavefunctions are $\Psi = Ae^{i(2mE)^{1/2}x/\hbar} + Be^{-i(2mE)^{1/2}x/\hbar}$, where *A* and *B* are constants and *E* is the energy of the particle. Is this wavefunction normalizable over the interval $-\infty < x < +\infty$? Explain the significance of your answer.

10.7 The Schrödinger Equation

10.25. Why does the Schrödinger equation have a specific operator for kinetic energy and only a general expression, *V*, for the potential energy?

10.26. Explain the reason that the kinetic energy operator part of the Schrödinger equation is a derivative whereas the potential energy operator part of the Schrödinger equation is simply "multiplication times a function *V*."

10.27. Use the Schrödinger equation to evaluate the total energy of a particle having mass *m* whose motion is described by the constant wavefunction $\Psi = k$. Assume $V = 0$. Justify your answer.

10.28. Evaluate the expression for the total energies for a particle having mass *m* and a wavefunction $\Psi = \sqrt{2} \sin \pi x$, if the potential energy *V* is 0 and if the potential energy *V* is 0.5 (assume arbitrary units). What is the difference between the two eigenvalues for the energy, and does this difference make sense?

10.29. Explain how the Hamiltonian operator is Hermitian. (See section 10.3 for the limitations of Hermitian operators.)

10.30. Verify that the following wavefunctions are indeed eigenfunctions of the Schrödinger equation, and determine their energy eigenvalues.

(a) $\Psi = e^{iKx}$ where $V = 0$ and *K* is a constant

(b) $\Psi = e^{iKx}$ where $V = k$, *k* is some constant potential energy, and *K* is a constant

(c) $\Psi = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a}$, where $V = 0$

10.31. In exercise 10.30a, the wavefunction is not normalized. Normalize the wavefunction and verify that it still satisfies the Schrödinger equation. The limits on x are 0 and 2π. How does the expression for the energy eigenvalue differ?

10.8 Particle-in-a-Box

10.32. Verify that equation 10.11 satisfies the Schrödinger equation, and that equation 10.12 gives the values for energy.

10.33. The electronic spectrum of the molecule butadiene, $CH_2{=}CH{-}CH{=}CH_2$, can be approximated using the one-dimensional particle-in-a-box if one assumes that the conjugated double bonds span the entire four-carbon chain. If the electron absorbing a photon having wavelength 2170 Å is going from the level $n = 2$ to the level $n = 3$, what is the approximate length of the C_4H_6 molecule? (The experimental value is about 4.8 Å.)

10.34. How many nodes are there for the one-dimensional particle-in-a-box in the state described by Ψ_5? by Ψ_{10}? by Ψ_{100}? Do not include the sides of the box as nodes.

10.35. Draw (at least roughly) the wavefunctions for the first five wavefunctions for the particle-in-a-box. Now draw the probabilities for the same wavefunctions. What similarities are there between the wavefunctions and their respective probabilities?

10.36. Show that the normalization constants for the general form of the wavefunction $\Psi = \sin(n\pi x/a)$ are the same and do not depend on the quantum number n.

10.37. Evaluate the probability that an electron will exist at the center of the box, approximated as $0.495a$ to $0.505a$, for the first, second, third, and fourth levels of a particle-in-a-box. What property of the wavefunction is apparent from your answers?

10.38. Is the uncertainty principle consistent with our description of the wavefunctions of the 1-D particle-in-a-box? (*Hint:* remember that position is not an eigenvalue operator for the particle-in-a-box wavefunctions.)

10.39. From drawings of the probabilities of particles existing in high-energy wavefunctions of a 1-D particle-in-a-box (like those shown in Figure 10.7), show how the correspondence principle indicates that, for high energies, quantum mechanics agrees with classical mechanics in that the particle is simply moving back and forth in the box.

10.40. Instead of $x = 0$ to a, assume that the limits on the 1-D box were $x = -(a/2)$ to $+(a/2)$. Derive acceptable wavefunctions for this particle-in-a-box. (You may have to consult an integral table to determine the normalization constant.) What are the quantized energies for the particle?

10.9 Average Values

10.41. Explain how $\Psi = \sqrt{2/a}\,\sin(n\pi x/a)$ isn't an eigenfunction of the position operator.

10.42. Evaluate the average value of position, $\langle x\rangle$, for Ψ_2 of a particle-in-a-box and compare it with the answer obtained in Example 10.12.

10.43. Evaluate $\langle p_x\rangle$ for Ψ_1 of a particle-in-a-box.

10.44. Evaluate $\langle E\rangle$ for Ψ_1 of a particle-in-a-box and show that it is exactly the same as the eigenvalue for energy obtained using the Schrödinger equation. Justify this conclusion.

10.45. Assume that for a particle on a ring the operator for the angular momentum, $\widehat{p_\phi}$, is $-i\hbar(\partial/\partial\phi)$. What is the eigenvalue for momentum for a particle having (unnormalized) Ψ equal to $e^{3i\phi}$? The integration limits are 0 to 2π. What is the average value of the momentum, $\langle p_\phi\rangle$ for a particle having this wavefunction? How are these results justified?

10.46. Mathematically, the uncertainty ΔA in some observable A is given by $\Delta A = \sqrt{\langle A^2\rangle - \langle A\rangle^2}$. Use this formula to determine Δx and Δp_x for $\Psi = \sqrt{2/a}\,\sin(\pi x/a)$ and show that the uncertainty principle holds.

10.11 & 10.12 3-D Particle-in-a-Box; Degeneracy

10.47. Why do we define $(1/X)(d^2/dx^2)X$ as $(-2mE/\hbar^2)$ and not simply as E?

10.48. What are the units on $(1/X)(d^2/dx^2)X$? Does this help explain your answer to the previous question?

10.49. Verify that the wavefunctions in equation 10.20 satisfy the three-dimensional Schrödinger equation.

10.50. An electron is confined to a box of dimensions 2Å × 3Å × 5Å. Determine the wavefunctions for the five lowest-energy states.

10.51. Assume a particle is confined to a cubical box. For what set of three quantum numbers will there first appear degenerate wavefunctions? For what sets of *different* quantum numbers will there first appear degenerate wavefunctions?

10.52. Determine the degeneracies of all levels for a cubical box from the lowest-energy wavefunction, described by the set of quantum numbers (1, 1, 1) to the wavefunction described by the quantum number set (4, 4, 4). *Hint:* you may have to use quantum numbers larger than 4 to determine proper degeneracies. See Example 10.15.

10.53. From the expressions for the 1-D and 3-D particles-in-boxes, suggest the forms of the Hamiltonian operator, acceptable wavefunctions, and the quantized energies of a particle in a two-dimensional box.

10.54. What are $\langle x\rangle$, $\langle y\rangle$, and $\langle z\rangle$ for Ψ_{111} of a 3-D particle-in-a-box? (The operators for y and z are similar to the operator for x, except that y is substituted for x wherever it appears, and the same for z.) What point in the box is described by these average values?

10.55. What are $\langle x^2\rangle$, $\langle y^2\rangle$, and $\langle z^2\rangle$ for Ψ_{111} of a 3-D particle-in-a-box? Assume that the operator $\widehat{x^2}$ is simply multiplication by x^2 and that the other operators are defined similarly. Check the integral table in Appendix 1 for needed integrals.

10.13 Orthogonality

10.56. Show that Ψ_{111} and Ψ_{112} for the 3-D particle-in-a-box are orthogonal to each other.

10.57. Verify that $\int \Psi_1^* \Psi_2 \, dx = \int \Psi_2^* \Psi_1 \, dx = 0$ for the 1-D particle-in-a-box, showing that the order of the wavefunctions inside the integral sign does not matter.

10.58. Evaluate the following integrals of the wavefunctions of particles-in-boxes by using equation 10.28 instead of solving the integrals:

(a) $\int \Psi_4^* \Psi_4 \, d\tau$

(b) $\int \Psi_3^* \Psi_4 \, d\tau$

(c) $\int \Psi_4^* \widehat{H} \Psi_4 \, d\tau$

(d) $\int \Psi_4^* \widehat{H} \Psi_2 \, d\tau$

(e) $\iiint \Psi_{111}^* \Psi_{111} \, d\tau$

(f) $\iiint \Psi_{111}^* \Psi_{121} \, d\tau$

(g) $\iiint \Psi_{111}^* \widehat{H} \Psi_{111} \, d\tau$

(h) $\iiint \Psi_{223}^* \widehat{H} \Psi_{322} \, d\tau$

10.14 Time-Dependent Schrödinger Equation

10.59. Substitute $\Psi(x, t) = e^{-iEt/\hbar} \cdot \Psi(x)$ into the time-dependent Schrödinger equation and show that it does solve that differential equation.

10.60. Write $\Psi(x, t) = e^{-iEt/\hbar} \cdot \Psi(x)$ in terms of sine and cosine, using Euler's theorem: $e^{i\theta} = \cos\theta + i \sin\theta$. What would a plot of $\Psi(x, t)$ versus time look like?

10.61. Evaluate $|\Psi(x, t)|^2$. How does it compare to $|\Psi(x)|^2$?

Symbolic Math Exercises

10.62. Construct plots of the probabilities of the first three wavefunctions for a particle in a one-dimensional box having length a. Identify where the nodes are.

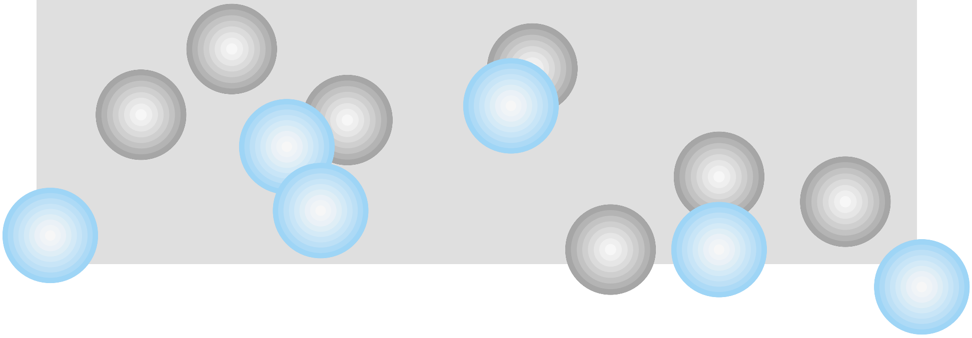
10.63. Numerically integrate the expression for the average value of position for Ψ_{10} for a particle-in-a-box and explain the answer.

10.64. Construct a table of energies of a particle in a 3-D box versus the quantum numbers n_x, n_y, and n_z, where the quantum numbers range from 1 to 10. Express the energies in $h^2/8ma^2$ units. Identify all examples of accidental degeneracies.

10.65. Numerically integrate the 1-D particle-in-a-box wavefunction product $\Psi_3{}^*\Psi_4$ over all space and show that the two functions are orthogonal.

11

Quantum Mechanics: Model Systems and the Hydrogen Atom



THE PREVIOUS CHAPTER INTRODUCED the basic postulates of quantum mechanics, illustrated key points, and applied the postulates to a simple ideal system, the particle-in-a-box. Although it is an ideally defined model system, the particle-in-a-box ideas are applicable to compounds having carbon-carbon double bonds like ethylene, and also to systems that have multiple conjugated double bonds, like butadiene, 1,3,5-hexatriene, and some dye molecules. The electrons in these systems do not act as perfect particles-in-a-box, but the model does a credible job of describing the energies in these molecules, certainly better than classical mechanics could describe them. Consider what quantum mechanics has provided so far: a simple, approximate, yet applicable description of electrons in some π bonds. This is more than anything classical mechanics provided.

Other model systems can be solved mathematically and exactly using the time-independent Schrödinger equation. In such systems, the Schrödinger equation is solved *analytically;* that is, by deriving a specific expression that yields exact answers (like the expressions for the wavefunctions and energies of the particle-in-a-box). Only for a few systems can the Schrödinger equation be solved analytically, and we will consider most of those. For all other systems, the Schrödinger equation must be solved numerically, by inserting numbers or expressions and seeing what answers come out. Quantum mechanics provides the tools for doing that, so don't let the rarity of analytic solutions shake the knowledge that quantum mechanics is the best theory for understanding the behavior of electrons and, therefore, atoms and molecules and chemistry in general.

11.1 Synopsis

We will consider the following systems, the behavior of which have exact, analytic solutions for Ψ in the Schrödinger equation:

- The harmonic oscillator, wherein a mass moves back and forth in a Hooke's-law type of motion and whose potential energy is proportional to the square of the displacement

- Two-dimensional rotational motion, which describes motion in a circular path
- Three-dimensional rotational motion, which describes motion on a spherical surface

We will conclude this chapter with a discussion of the hydrogen atom. Recall that Bohr's theory described the hydrogen atom, and correctly predicted its spectrum. However, Bohr's theory was based on some assumptions that, when applied, provided the right answer. Quantum mechanics has its postulates, and we will see that it, too, predicts the same spectrum for the hydrogen atom. In order to be a superior theory, quantum mechanics must not only do the same things as earlier theories but do more. In the next chapter, we will see how quantum mechanics is applied to systems larger than hydrogen (and most systems of interest are considerably larger than hydrogen!), thereby making it a better description of matter.

11.2 The Classical Harmonic Oscillator

The classical *harmonic oscillator* is a repetitive motion that follows Hooke's law. For some mass m, Hooke's law states that for a one-dimensional displacement $\mathbf{x}$ from some equilibrium position, the force $\mathbf{F}$ acting against the displacement (that is, the force that is acting to return the mass to the equilibrium point) is proportional to the displacement:

$$\mathbf{F} = -k\mathbf{x} \tag{11.1}$$

where k is called the *force constant.* Note that both $\mathbf{F}$ and $\mathbf{x}$ are vectors, and the negative sign in the equation indicates that the force and displacement vectors are opposite in direction. Since force has typical units of newtons or dynes and displacement has units of distance, the force constant can have units like N/m or, in other units that sometimes yield more manageable numbers, millidynes per angstrom (mdyn/Å).

The potential energy, denoted V, of a Hooke's-law harmonic oscillator is related to the force by a simple integral. The relationship and final result are

$$V = -\int \mathbf{F}\, d\mathbf{x} = \tfrac{1}{2}k\mathbf{x}^2$$

To simplify our presentation, we ignore the vector characteristic of the position and focus on its magnitude, x. Since x is squared in the expression for V, negative values of x don't need to be treated in any special fashion. The resulting working equation for the potential energy of a harmonic oscillator is more simply written as

$$V = \tfrac{1}{2}kx^2 \tag{11.2}$$

The potential energy does not depend on the mass of the oscillator. A plot of this potential energy is shown in Figure 11.1.*

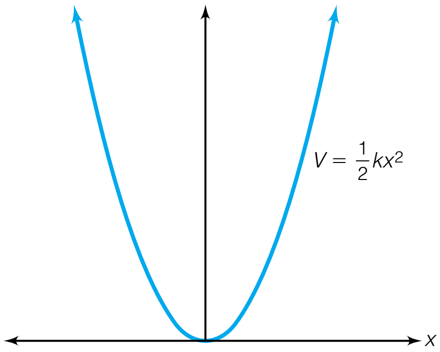


Figure 11.1 A plot of the potential energy diagram $V(x) = \frac{1}{2}kx^2$ for an ideal harmonic oscillator.

Classically, the behavior of the ideal harmonic oscillator is well known. The position of the oscillator versus time, $x(t)$, is

$$x(t) = x_0 \sin\left(\sqrt{\frac{k}{m}}t + \phi\right)$$

where x_0 is the maximum amplitude of the oscillation, k and m are the force constant and mass, t is time, and ϕ is some *phase factor* (which indicates the

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*An *anharmonic oscillator* is one that does not follow Hooke's law and, ultimately, does not have a potential energy as defined in equation 11.2. Anharmonic oscillators are discussed in a later chapter.

absolute position of the mass at the starting time, when $t = 0$). We get this equation by solving the appropriate equations of motion, whether expressed in Newton's or Lagrange's or Hamilton's format.

It takes a certain time, τ seconds, for the oscillator to complete one full cycle. Therefore, in 1 second, there will be $1/\tau$ oscillations. In a sinusoidal motion, one cycle corresponds to an angular change of 2π. The *frequency* of the oscillator in number of cycles per second or simply 1/second (s^{-1}; another SI-approved name for s^{-1} is *hertz,* or Hz) is defined as ν (Greek *nu*) and is equal to

$$\nu = \frac{1}{\tau} = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \tag{11.3}$$

The frequency ν is independent of the displacement. Such relationships have been known since the late 1600s. Familiar harmonic oscillators include masses on springs and clock pendulums.

Example 11.1

Assuming units of N/m for the force constant and kg for mass, verify that equation 11.3 yields units of s^{-1} for frequency.

Solution

Recall that newton is a composite unit and that

$$1\ \text{N} = 1\ \frac{\text{kg}\cdot\text{m}}{\text{s}^2}$$

The basic units for k are therefore

$$\frac{\text{kg}\cdot\text{m}}{\text{s}^2} \div \text{m} = \frac{\text{kg}\cdot\text{m}}{\text{m}\cdot\text{s}^2} = \frac{\text{kg}}{\text{s}^2}$$

Since the $1/2\pi$ term doesn't have any units associated with it, the units from equation 11.3 become

$$\sqrt{\frac{\text{kg/s}^2}{\text{kg}}} = \sqrt{\frac{1}{\text{s}^2}} = \frac{1}{\text{s}} = \text{s}^{-1}$$

thus confirming that the frequency ν has units of s^{-1}.

Example 11.2

a. For small displacements, a clock's pendulum can be treated as a harmonic oscillator. A pendulum has a frequency of 1.00 s^{-1}. If the mass of the pendulum is 5.00 kg, what is the force constant acting on the pendulum in units of N/m? What is this force constant in units of mdyn/Å?

b. Calculate the similar force constant for a hydrogen atom having mass 1.673×10^{-27} kg, attached to an atomically flat metal surface and vibrating with a frequency of $6.000 \times 10^{13}\ s^{-1}$.

Solution

a. One need simply substitute into equation 11.3. Using units consistent with N/m for the force constant, the equation looks like this:

$$1.00\ \text{s}^{-1} = \frac{1}{2\pi}\sqrt{\frac{k}{5.00\ \text{kg}}}$$

The expression is rearranged to solve for k, and the result is 197 N/m. There are 10^5 dynes per newton, 1000 mdyn per dyne, and 10^{10} Å per meter, so it is easy to show that this is equal to 1.97 mdyn/Å.

b. In the second case, again using equation 11.3:

$$6.000 \times 10^{13}\ \mathrm{s}^{-1} = \frac{1}{2\pi}\sqrt{\frac{k}{1.673 \times 10^{-27}\ \mathrm{kg}}}$$

Evaluating this, one gets 237.8 N/m, which equals 2.378 mdyn/Å.

11.3 The Quantum-Mechanical Harmonic Oscillator

Quantum mechanically, a wavefunction for a one-dimensional harmonic oscillator can be determined using the (time-independent) Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \hat{V}(x)\right]\Psi = E\Psi$$

The potential energy for the quantum-mechanical system has the same form as the potential energy for the classical system. (Generally speaking, since potential energies are energies of *position,* the quantum-mechanical form of the potential energy is the same as the classical form. But now because of the form of the Schrödinger equation, the potential energy *operator* is multiplied by the wavefunction Ψ.) The Schrödinger equation for the harmonic oscillator is

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right]\Psi = E\Psi \tag{11.4}$$

and acceptable wavefunctions for this one-dimensional system must satisfy this eigenvalue equation.

This differential equation does have an analytic solution. The method we use here is one general technique for solving differential equations: we define the wavefunction as a power series. What we will ultimately find is that in order to solve the Schrödinger equation, the power series must have a special form.

First, the Schrödinger equation 11.4 will be rewritten using equation 11.3 to substitute for k. Rearranging equation 11.3, one finds that the force constant k is

$$k = 4\pi^2\nu^2 m \tag{11.5}$$

and so the Schrödinger equation for a one-dimensional harmonic oscillator becomes

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + 2\pi^2\nu^2 mx^2\right]\Psi = E\Psi$$

Now we will do three things. First, we define

$$\alpha \equiv \frac{2\pi\nu m}{\hbar}$$

Second, we divide both sides of the equation by the term $-\hbar^2/2m$. Third, we bring all terms over to one side of the equation so that we have an expression equaling zero. The Schrödinger equation becomes

$$\left[\frac{d^2}{dx^2} - \alpha^2x^2\right]\Psi + \frac{2mE}{\hbar^2}\Psi = 0$$

or

$$\frac{d^2\Psi}{dx^2} + \left(\frac{2mE}{\hbar^2} - \alpha^2x^2\right)\Psi = 0 \tag{11.6}$$

where equation 11.6 has been rearranged from the previous expression to show in parentheses the two terms that are simply being multiplied by Ψ. The first term is the second derivative of Ψ.

We now assume that the form of the wavefunction Ψ that satisfies this Schrödinger equation has the form of a power series in the variable x. That is, the wavefunction is some function $f(x)$ that has some term containing x^0 (which is simply 1), some term containing x^1, some term containing x^2, ad infinitum, all added together. Each power of x has some constant called a *coefficient* multiplying it, so the form of $f(x)$ (recognizing that $x^0 = 1$) is:

$$f(x) = c_0 + c_1x^1 + c_2x^2 + c_3x^3 + \cdots$$

The c's are the coefficients multiplying the powers of x. It is more concise to write the above function using standard summation notation, as in the following:

$$f(x) = \sum_{n=0}^{\infty} c_nx^n \tag{11.7}$$

where n is the *index* of the summation. For now, the summation goes to infinity. This causes a potential problem, because sums that go to an infinite number of terms often approach infinity themselves unless there is a way for each successive term to become smaller and smaller. A partial solution is to assume that every term in the sum is multiplied by another term that gets much smaller as x itself (and therefore x^n) gets larger. The term that will work in this case is $e^{-\alpha x^2/2}$. (Note the inclusion of the constant α here. You may wonder why we use this particular exponential function. At this point, the only justification for using this function is that it will yield an analytic solution.) This exponential is an example of a *Gaussian-type function* (named after the eighteenth- to ninteenth-century mathematician Karl Friedrich Gauss). The wavefunction for this system is now

$$\Psi = e^{-\alpha x^2/2} \cdot f(x) \tag{11.8}$$

where $f(x)$ is the power series defined in equation 11.7.

At this point, the first and then the second derivative can be determined with respect to x. Then the expressions for the second derivative as well as the original function can be substituted into the proper form of the Schrödinger equation, equation 11.6. Once we do so, the logic behind the choice of the exponential function $e^{-\alpha x^2/2}$ will become apparent mathematically. Using the product rule of differentiation, the first derivative is

$$\Psi' = (-\alpha x)e^{-\alpha x^2/2} \cdot f(x) + e^{-\alpha x^2/2} \cdot f'(x)$$

where Ψ' and $f'(x)$ refer to the first derivatives of Ψ and $f(x)$ with respect to x. Using the above equation, the second derivative of Ψ with respect to x can be determined using the product rule. It is, after doing a little algebra:

$$\Psi'' = e^{-\alpha x^2/2}[\alpha^2x^2f(x) - \alpha f(x) - 2\alpha xf'(x) + f''(x)] \tag{11.9}$$

Here $e^{-\alpha x^2/2}$ has been factored out of every term in the second derivative. Substituting the forms of Ψ and Ψ'' into the form of the Schrödinger equation given by equation 11.6 yields

$$e^{-\alpha x^2/2}[\alpha^2x^2f(x) - \alpha f(x) - 2\alpha xf'(x) + f''(x)] + \left(\frac{2mE}{\hbar^2} - \alpha^2x^2\right)e^{-\alpha x^2/2} \cdot f(x) = 0 \tag{11.10}$$

Every term in equation 11.10 has the exponential $e^{-\alpha x^2/2}$ in it, so it can be algebraically divided out. Its residual influence on equation 11.10, in the form of the α's and x's in the second derivative expression, is obvious. Further, the terms in $f(x)$, $f'(x)$, and $f''(x)$ can be grouped together and simplified so that the substituted Schrödinger equation becomes [omitting the (x) part of the power series f]

$$f'' - 2\alpha x f' + \left(\frac{2mE}{\hbar^2} - \alpha\right) f = 0 \qquad \textbf{(11.11)}$$

This equation has terms arising from the power series f, its first derivative f', and its second derivative f''. The terms in $\alpha^2 x^2 \cdot f$ have canceled. Since we are assuming that f is a power series, we can actually write out, term by term, what the derivatives are. Rewriting the original power series first, the derivatives are

$$f(x) = \sum_{n=0}^{\infty} c_n x^n \qquad \text{(from 11.7 above)}$$

$$f' = \sum_{n=1}^{\infty} n c_n x^{n-1}$$

$$f'' = \sum_{n=2}^{\infty} n(n-1) c_n x^{n-2}$$

The constants c_n are unaffected by the derivation, since they are constants. The starting value of the index n changes with each derivative. In the first derivative, since the first term of the original function f is constant, we lose the $n = 0$ term. Now the $n = 1$ term is a constant, since the power of x for the $n = 1$ term is now 0, that is, $x^{1-1} = x^0 = 1$. In the second derivative, the $n = 1$ term, a constant in the f' expansion, itself becomes zero for the second derivative, and so the summation starts at $n = 2$. You should satisfy yourself that this is indeed the case, and that the above three expressions with the given summation boundaries are correct (of course, the infinity boundary does not change).

Since the first term in the summation for f becomes 0 in f', the first derivative f' does not change if we add a 0 as a first term and then start the summation at $n = 0$. Understand that this does not change f', since the first term, the $n = 0$ term, is simply zero. But this does allow us to start the summation at $n = 0$ instead of $n = 1$ (the importance of this will be seen shortly). Therefore, we can write f' as

$$f' = \sum_{n=0}^{\infty} n c_n x^{n-1} \qquad \textbf{(11.12)}$$

Again, this does not change the power series itself; it only changes the initial value of the index n. The same tactic *can* be taken with f'', but mathematically this will not lead anywhere. Rather, by doing a two-step *redefinition of the index,* we can achieve much more. Since the index n is simply a counting number used to label the terms in the power series, we can shift the index by simply redefining, say, an index i as $i \equiv n - 2$. Since this means that $n = i + 2$, the expression for the second derivative f'' can be rewritten by substituting for every n:

$$f'' = \sum_{i+2=2}^{\infty} (i+2)(i+2-1) c_{i+2} x^{i+2-2}$$

which simply becomes

$$f'' = \sum_{i=0}^{\infty} (i+2)(i+1) c_{i+2} x^{i}$$

Mathematically, the function f'' has not changed. What has changed is the index, which has shifted by 2. It is the same second derivative function determined originally.

Of course, it doesn't matter what letter is used to designate the index. If that is the case, why not use n? The second derivative f'' becomes

$$f'' = \sum_{n=0}^{\infty}(n+2)(n+1)c_{n+2}x^n \tag{11.13}$$

which is the useful form of the second derivative.

The reason all this manipulation has taken place is so that when the summations are substituted into the Schrödinger equation, all terms can be grouped under the same summation sign (and this cannot be done unless the summation index starts at the same number and means the same thing in all expressions). Now the summations for f, f', and f'' can be substituted into equation 11.11. The resulting equation is

$$\sum_{n=0}^{\infty}(n+2)(n+1)c_{n+2}x^n - 2\alpha x\sum_{n=0}^{\infty}nc_nx^{n-1} + \left(\frac{2mE}{\hbar^2} - \alpha\right)\sum_{n=0}^{\infty}c_nx^n = 0$$

Because all of the summations in the above equation start at zero, go to infinity, and use the same index, it can be rewritten as a single summation. This is the reason for getting the indices to be the same for all summations. The equation becomes

$$\sum_{n=0}^{\infty}\left[(n+2)(n+1)c_{n+2}x^n - 2\alpha xnc_nx^{n-1} + \left(\frac{2mE}{\hbar^2} - \alpha\right)c_nx^n\right] = 0$$

This equation can be simplified by recognizing that the x's in the second term can be combined so that the power on x becomes n, and further recognizing that all three terms now have x raised to the power of n. Making the combination and factoring x^n out of all terms yields

$$\sum_{n=0}^{\infty}\left[(n+2)(n+1)c_{n+2} - 2\alpha nc_n + \left(\frac{2mE}{\hbar^2} - \alpha\right)c_n\right]x^n = 0 \tag{11.14}$$

Now we need to determine the values of the constants c_n. Recall that this equation was determined by substituting a trial wavefunction into the Schrödinger equation, so that if the harmonic oscillator system has wavefunctions that are eigenfunctions of the Schrödinger equation, those wavefunctions would be of the form given in equation 11.8 [that is, $\Psi = e^{-\alpha x^2/2} \cdot f(x)$]. By identifying the constants, we complete our determination of the wavefunctions of a harmonic oscillator.

Equation 11.14 is an infinite sum that equals exactly zero. This is a somewhat remarkable conclusion: if one were to add up all infinite terms in the sum, the total would be exactly zero. The only way to guarantee this for all values of x is if *every* coefficient multiplying x^n in equation 11.14 were *exactly* zero:

$$(n+2)(n+1)c_{n+2} - 2\alpha nc_n + \left(\frac{2mE}{\hbar^2} - \alpha\right)c_n = 0 \qquad \text{for any } n$$

This does not mean that every coefficient c_n is exactly zero [that would imply that our power series $f(x)$ is exactly zero]. It means that the *entire expression* above must be zero. This requirement allows us to rewrite the above equation to get a relationship between one coefficient c_n and the coefficient two places away, c_{n+2}.

$$c_{n+2} = \frac{\alpha + 2\alpha n - 2mE/\hbar^2}{(n+2)(n+1)} c_n \tag{11.15}$$

An equation that relates sequential coefficients like this is called a *recursion relation.* It allows one to determine successive coefficients, knowing the previous ones. Ultimately, only two constants need be known at the outset: c_0, from which the even-powered coefficients $c_2, c_4, c_6, \ldots$ can be determined, and c_1, from which the odd-powered coefficients $c_3, c_5, c_7, \ldots$ can be determined.

Now one of the requirements for proper wavefunctions can be applied: they must be *bounded.* Although this derivation started by assuming an infinite series as a solution, the wavefunction cannot be infinite and still apply to reality. Even the inclusion of the $e^{-\alpha x^2/2}$ term does not guarantee that the infinite sum will be bounded. But the recursion relation in equation 11.15 provides a way to get this guarantee. Because the coefficient c_{n+2} depends on c_n, if for some n the coefficient c_n is exactly zero, all successive constants $c_{n+2}, c_{n+4}, c_{n+6}, \ldots$ are also exactly zero. Of course, this does not affect the other coefficients c_{n+1}, $c_{n+3}, \ldots$. So, in order to guarantee a bounded wavefunction, we must first separate the odd and even terms into two separate power series:

$$f_{\text{even}} = \sum_{n=0}^{\infty,\ \text{even}} c_n x^n$$

$$f_{\text{odd}} = \sum_{n=1}^{\infty,\ \text{odd}} c_n x^n$$

We will require that the wavefunctions themselves be composed of $e^{-\alpha x^2/2}$ times *either* a sum of only odd terms *or* a sum of only even terms. For each sum it is now required that, in order for the wavefunction to not be infinite, at some value of n the next coefficient c_{n+2} must become zero. That way, all further coefficients will also be zero. Since the coefficient c_{n+2} can be calculated from the previous constant c_n due to the recursion relation, we can substitute zero for c_{n+2}:

$$0 = \frac{\alpha + 2\alpha n - 2mE/\hbar^2}{(n+2)(n+1)} c_n$$

The only way for the coefficient c_{n+2} to become identically zero is if the numerator of the fraction in the above equation becomes zero at that value of n:

$$\alpha + 2\alpha n - \frac{2mE}{\hbar^2} = 0$$

This expression includes the total energy E of the harmonic oscillator. Energy is an important observable, so let us detour to consider it. In order for the wavefunction to be noninfinite, the energy of the harmonic oscillator, when combined with the other terms like α, n, m, and $\hbar$, must have only those values that satisfy the above equation. Therefore, we can solve for what the values of the energy must be. Substituting also for $\alpha \equiv 2\pi\nu m/\hbar$, we find a simple conclusion:

$$E = (n + \tfrac{1}{2})h\nu \tag{11.16}$$

where n is the value of the index where the next coefficient of the series becomes zero, h is Planck's constant, and ν is the classical frequency of the oscillator. That is, the total energy of the harmonic oscillator depends *only* on its classical frequency (determined by its mass and force constant), Planck's constant, and some integer n. Since the energy can have values only as determined by this equation, the total energy of the harmonic oscillator is *quantized.* The

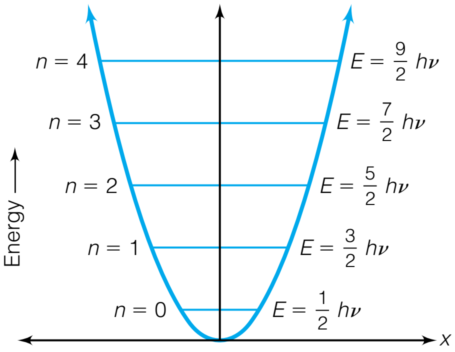


Figure 11.2 A diagram of the energy levels of an ideal harmonic oscillator, as predicted by the solutions to the Schrödinger equation. Note that the lowest quantized level, $E(n = 0)$, does not have zero energy.

index n is the *quantum number,* and it can have any integer value from 0 to infinity. (As we will see from the form of the wavefunction, 0 is a possible value for the quantum number in this case.)

Before returning to wavefunctions, we have a few points to consider with respect to the total energy. A diagram of the energy levels for different quantum numbers (assuming the mass and the force constant remain the same) is shown in Figure 11.2. For an ideal harmonic oscillator, the energy levels are spaced by the same amount. It is easy to show that the energy levels are separated by $\Delta E = h\nu$. Further, the lowest possible value for energy is not zero. This is seen by substituting the lowest possible value for the quantum number n, which is zero. We get

$$E(n = 0) = (0 + \tfrac{1}{2})h\nu = \tfrac{1}{2}h\nu$$

which is a nonzero value for the total energy. This introduces the concept of *zero-point energy.* At the minimum value for the quantum number (the *ground state* of the oscillator), there is still a *nonzero* amount of energy in the system.

The frequency, ν, should be in units of s^{-1}. Multiplying s^{-1} by the units on Planck's constant, J·s or erg·s, results in units of J or erg, which are units of energy. It is common to express the energy difference in terms of the photon used to excite a system from one energy level to another, since harmonic oscillators can go from state to state by the absorption or emission of a photon, just as with Bohr's hydrogen atom. One characteristic used to describe the photon is its wavelength. Using the equation $c = \lambda\nu$ (where c is the speed of light and λ is its wavelength), one can convert from wavelength to frequency. The following examples illustrate.

Example 11.3

A single oxygen atom attached to a smooth metal surface vibrates at a frequency of $1.800 \times 10^{13}\ \mathrm{s}^{-1}$. Calculate its total energy for the $n = 0$, 1, and 2 quantum numbers.

Solution:

We use equation 11.16 with $\nu = 1.800 \times 10^{13}\ \mathrm{s}^{-1}$ and $n = 0$, 1, and 2:

$$E(n = 0) = (0 + \tfrac{1}{2})(6.626 \times 10^{-34}\ \mathrm{J{\cdot}s})(1.800 \times 10^{13}\ \mathrm{s}^{-1})$$
$$E(n = 1) = (1 + \tfrac{1}{2})(6.626 \times 10^{-34}\ \mathrm{J{\cdot}s})(1.800 \times 10^{13}\ \mathrm{s}^{-1})$$
$$E(n = 2) = (2 + \tfrac{1}{2})(6.626 \times 10^{-34}\ \mathrm{J{\cdot}s})(1.800 \times 10^{13}\ \mathrm{s}^{-1})$$

From the above expressions, we get

$$E(n = 0) = 5.963 \times 10^{-21}\ \mathrm{J}$$
$$E(n = 1) = 1.789 \times 10^{-20}\ \mathrm{J}$$
$$E(n = 2) = 2.982 \times 10^{-20}\ \mathrm{J}$$

The minimum energy of this vibrating oxygen atom, its zero-point energy, is 5.963×10^{-21} J.

Example 11.4

Calculate the wavelength of light necessary to excite a harmonic oscillator from one energy state to the adjacent higher state in Example 11.3. Express the wavelength in units of m, µm (micrometers), and Å.

Solution

The difference in energy of the adjacent states is the same and equals $h\nu$, or

$$\Delta E = (6.626 \times 10^{-34}\ \text{J·s})(1.800 \times 10^{13}\ \text{s}^{-1}) = 1.193 \times 10^{-20}\ \text{J}$$

Since the energy of a photon is given by the equation $E = h\nu$, the calculation can be reversed to obtain the frequency of the photon necessary. It should be obvious that the frequency of the photon is thus $1.800 \times 10^{13}\ \text{s}^{-1}$. Using the equation $c = \lambda\nu$:

$$2.9979 \times 10^{8}\ \text{m/s} = \lambda(1.800 \times 10^{13}\ \text{s})$$

$$\lambda = 0.00001666\ \text{m} = 1.666 \times 10^{-5}\ \text{m}$$

This corresponds to 16.66 μm or 166,600 Å. Calculations using the equations $E = h\nu$ and $c = \lambda\nu$ are common in physical chemistry. Students should always remember that these equations can be used to convert quantities like E, ν, and λ to corresponding values with other units.

11.4 The Harmonic Oscillator Wavefunctions

We return to the wavefunction itself. It has already been established that the wavefunction is an exponential $e^{-\alpha x^2/2}$ times a power series that has been argued to have a limited, not an infinite, number of terms. The final term in the sum is determined by the value of the quantum number n, which also specifies the total energy of the oscillator. Further, each wavefunction is composed of either all odd powers of x in the power series, or all even powers of x. The wavefunctions can be represented as

$$\begin{aligned}
\Psi_0 &= e^{-\alpha x^2/2}(c_0)\\
\Psi_1 &= e^{-\alpha x^2/2}(c_1 x)\\
\Psi_2 &= e^{-\alpha x^2/2}(c_0 + c_2 x^2)\\
\Psi_3 &= e^{-\alpha x^2/2}(c_1 x + c_3 x^3)\\
\Psi_4 &= e^{-\alpha x^2/2}(c_0 + c_2 x^2 + c_4 x^4)\\
\Psi_5 &= e^{-\alpha x^2/2}(c_1 x + c_3 x^3 + c_5 x^5)\\
&\vdots
\end{aligned} \tag{11.17}$$

It should be pointed out that the c_0 constant in Ψ_0 does not have the same value as the c_0 in Ψ_2 or Ψ_4, or other Ψ's. This is also true for the values of c_1, c_2, and so on, in the expansions of the summations. The first wavefunction, Ψ_0, consists only of the exponential term multiplied by the constant c_0. This nonzero wavefunction is what allows a quantum number of 0 to be allowed for this system, unlike the situation for the particle-in-a-box. All the other wavefunctions consist of the exponential term multiplied by a power series in x that is composed of one or more terms. Instead of an infinite power series, this set of terms is simply a *polynomial.*

Like any proper wavefunction, these wavefunctions must be normalized. The wavefunction Ψ_0 is easiest to normalize since it has only a single term in its polynomial. The range of the one-dimensional harmonic oscillator is $-\infty$ to $+\infty$, since there is no restriction on the possible change in position.

To normalize, the wavefunction Ψ_0 must be multiplied by some constant N such that

$$N^2 \int_{-\infty}^{+\infty} (c_0 e^{-\alpha x^2/2})^*(c_0 e^{-\alpha x^2/2})\, dx = 1 \tag{11.18}$$

Since N and c_0 are both constants, it is customary to combine them into a single constant N. The complex conjugate of the exponential does not change the form of the exponential, since it does not contain the imaginary root i. The integral becomes

$$N^2 \int_{-\infty}^{+\infty} e^{-\alpha x^2}\, dx = 1$$

The final change to this integral begins with the understanding that because the x in the exponential is squared, the negative values of x yield the same values of $e^{-\alpha x^2}$ as do the positive values of x. This is one way of defining an *even* mathematical function. [Formally, $f(x)$ is even if, for all x, $f(-x) = f(x)$. For an *odd* function, $f(-x) = -f(x)$. Examples of simple odd and even functions are shown in Figure 11.3.] The fact that the above exponential has the same values for negative values of x as for positive values of x means that the integral from $x = 0$ to $-\infty$ is equal to the integral from $x = 0$ to $+\infty$. So instead of our interval being $x = -\infty$ to $+\infty$, let us take it as $x = 0$ to $+\infty$ and take *twice* the value of that integral. The normalization expression becomes

$$2 \cdot N^2 \int_{0}^{+\infty} e^{-\alpha x^2}\, dx = 1$$

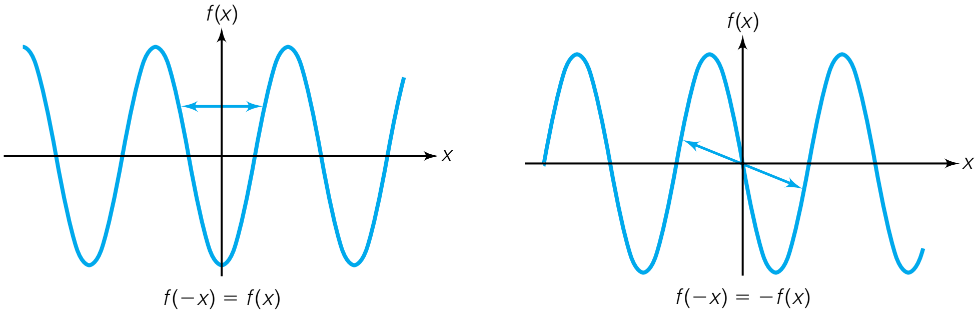
The integral $\int_0^{+\infty} e^{-\alpha x^2}\, dx$ has a known value, $\frac{1}{2}(\frac{\pi}{a})^{1/2}$. In this case, $a \equiv \alpha$. Substituting for this and solving for N, one finds

$$N = \left(\frac{\alpha}{\pi}\right)^{1/4}$$

The complete wavefunction Ψ_0 is therefore

$$\Psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

It turns out that the set of harmonic oscillator wavefunctions were already known. This is because differential equations like those of equation 11.6, the rewritten Schrödinger equation, had been studied and solved mathematically



(a) **(b)**

Figure 11.3 Examples of odd and even functions. (a) This function is even, so that changing the sign on x (from x to $-x$) yields the same value as for $f(x)$, as the arrow shows. (b) This function is odd, where changing the sign on x yields $-f(x)$, as the arrow shows.

before quantum mechanics was developed. The polynomial parts of the harmonic oscillator wavefunctions are called *Hermite polynomials* after Charles Hermite, the nineteenth-century French mathematician who studied their properties. For convenience, if we define $\xi \equiv \alpha^{1/2}x$ (where ξ is the Greek letter *xi*, pronounced "zigh"), then the Hermite polynomial whose largest power of x is n is labeled $H_n(\xi)$. The first few $H_n(\xi)$ polynomials are listed in Table 11.1, and Table 11.2 gives the solutions to an integral involving the Hermite polynomials. Tables 11.1 and 11.2 should be used with care because of the variable change. The following example illustrates some of the potential pitfalls in using tabulated Hermite polynomials.

Table 11.1 The first six Hermite polynomials[a]

n	$H_n(\xi)$
0	1
1	2ξ
2	$4\xi^2 - 2$
3	$8\xi^3 - 12\xi$
4	$16\xi^4 - 48\xi^2 + 12$
5	$32\xi^5 - 160\xi^3 + 120\xi$
6	$64\xi^6 - 480\xi^4 + 720\xi^2 - 120$

[a] In the treatment of the harmonic oscillator, note that $\xi = \alpha^{1/2}x$.

Table 11.2 Integral involving Hermite polynomials

$$\int_{-\infty}^{+\infty} H_a(\xi)^* H_b(\xi) e^{-\xi^2}\, d\xi = \begin{cases} 0 \text{ if } a \neq b \\ 2^a a!\pi^{1/2} \text{ if } a = b \end{cases}$$

Example 11.5

Using the integrals in Table 11.2, normalize Ψ_1 for a quantum-mechanical harmonic oscillator.

Solution

The integral from Table 11.2 will have to be used with care, because of the differences in the variables between the equation in the table and the wavefunction Ψ_1. If $\xi \equiv \alpha^{1/2}x$, then $d\xi = \alpha^{1/2}\,dx$, and after substitution for ξ and $d\xi$ the integral can be applied directly. The normalization requirement means, mathematically,

$$\int_{-\infty}^{+\infty} \Psi^*\Psi\, dx = 1$$

The limits on the integral are $+\infty$ and $-\infty$, and the infinitesimal is dx for the one-dimensional integrand. For the Ψ_1 wavefunction of the harmonic oscillator, it is assumed that the wavefunction is multiplied by some constant N such that

$$N^2 \int_{-\infty}^{+\infty} [H_1(\alpha^{1/2}x) \cdot e^{-\alpha x^2/2}]^* \cdot H_1(\alpha^{1/2}x) \cdot e^{-\alpha x^2/2}\, dx = 1$$

Substituting for ξ and $d\xi$, this is transformed into

$$N^2 \int_{-\infty}^{+\infty} [H_1(\xi) \cdot e^{-\xi^2/2}]^* \cdot H_1(\xi) \cdot e^{-\xi^2/2}\, \frac{d\xi}{\alpha^{1/2}} = 1$$

The complex conjugate does not change the wavefunction and so can be ignored. $\alpha^{1/2}$ is a constant and can be moved outside the integral. The functions inside the integral sign are all multiplied together, and so the integral can be simplified to

$$\frac{N^2}{\alpha^{1/2}} \int_{-\infty}^{+\infty} H_1(\xi) \cdot H_1(\xi) \cdot e^{-\xi^2}\, d\xi = 1$$

According to Table 11.2, this integral has a known form and, for $n = 1$, equals $2^1 1!\pi^{1/2}$ (where ! indicates a factorial). Therefore,

$$\frac{N^2}{\alpha^{1/2}} \cdot 2^1 1!\pi^{1/2} = 1$$

$$N^2 = \frac{\alpha^{1/2}}{2\pi^{1/2}}$$

$$N = \frac{\alpha^{1/4}}{\sqrt{2}\pi^{1/4}}$$

By convention, only the positive square root is used. The $\sqrt{2}$ in the expression above is usually converted into the fourth root of 4 (that is, $\sqrt[4]{4}$, or $4^{1/4}$) so that all of the powers can be combined and the normalization constant can be rewritten as

$$N = \left(\frac{\alpha}{4\pi}\right)^{1/4}$$

The complete wavefunction for the $n = 1$ level is, after resubstituting in terms of x:

$$\Psi_1 = \left(\frac{\alpha}{4\pi}\right)^{1/4} H_1(\alpha^{1/2}x) \cdot e^{-\alpha x^2/2}$$

The normalization constants for the harmonic oscillator wavefunctions Ψ_n follow a certain pattern (largely because the formulas for the integrals involve Hermite polynomials) and so can be expressed as a formula. The general formula for the harmonic oscillator wavefunctions given below includes an expression for the normalization constant in terms of the quantum number n:

$$\Psi(n) = \left(\frac{\alpha}{\pi}\right)^{1/4} \cdot \left(\frac{1}{2^n n!}\right)^{1/2} \cdot H_n(\alpha^{1/2}x) \cdot e^{-\alpha x^2/2} \tag{11.19}$$

where all of the terms have been previously defined.

Determining whether a function is odd or even can sometimes be useful, since for an odd function ranging from $+\infty$ to $-\infty$ and centered at $x = 0$, the integral of that function is identically zero. After all, what is an integral but an area under a curve? For an odd function, the positive area of one half of the curve is canceled out by the negative area of the other half. Recognizing this eliminates the need to mathematically evaluate an integral. Determining whether a product of functions is odd or even depends on the individual functions themselves, since (odd) × (odd) = (even), (even) × (even) = (even), and (even) × (odd) = (odd). This mimics the rules for multiplication of positive and negative numbers. The following example illustrates how to take advantage of this.

Example 11.6

Evaluate $\langle x\rangle$ for Ψ_3 of a harmonic oscillator by inspection. That is, evaluate by considering the properties of the functions instead of calculating the average value mathematically.

Solution

The average value of the position of the harmonic oscillator in the state Ψ_3 can be determined using the formula

$$\langle x\rangle = N^2 \int_{-\infty}^{+\infty} [H_3(\xi) \cdot e^{-\alpha x^2/2}]^* \hat{x} [H_3(\xi) \cdot e^{-\alpha x^2/2}]\, dx$$

where N is the normalization constant and no substitution has been made for the variable x (and it will not matter). This can be simplified, especially by remembering that the position operator $\hat{x}$ is multiplication by the coordinate x, and all other parts of the integrand are being multiplied together:

$$\langle x\rangle = N^2 \int_{-\infty}^{+\infty} x \cdot [H_3(\xi)]^2 \cdot e^{-\alpha x^2}\, dx$$

The Hermite polynomial $H_3(\xi)$ contains only odd powers of x, but upon squaring it becomes a polynomial having only even powers of x. Therefore, it is an even function. The exponential has x^2 in it, so it is an even function. The term x itself is an *odd* function. (The dx is not considered, since it is part of the integration operation, not a function.) Therefore the overall function is odd, and the integral itself, centered at zero and going from $-\infty$ to $+\infty$, is identically zero. Therefore $\langle x \rangle = 0$.

This property of odd functions is extremely useful. For even functions, the integral *must* be evaluated. Probably the best method of doing so at this point is to substitute for the form of the Hermite polynomial, multiply out the terms, and evaluate each term according to its form. Several integrals from Appendix 1 may be useful. However, odd functions integrated over the proper interval are exactly zero, and such a determination can be made by an inspection of the function rather than evaluation of the integral—a timesaving routine, when possible.

Plots of the first few harmonic-oscillator wavefunctions are shown in Figure 11.4. Superimposed with them is the potential energy curve of a harmonic oscillator. Although the exact dimensions of Figure 11.4 depend on what m and k are, the general conclusions do not. Recall that in a classical harmonic oscillator, a mass goes back and forth about a center. When passing the $x = 0$ center, the mass has minimum potential energy (which can be set to zero) and maximum kinetic energy. It is moving at its fastest speed. As the mass extends farther away from the center, the potential energy grows until all of the energy is potential, none is kinetic, and the mass momentarily stops. Then it begins motion in the other direction. The point at which the mass turns around is called the *classical turning point.* A classical harmonic oscillator never extends beyond its turning point, since that would mean that it has more potential energy than total energy.

As seen in Figure 11.4, wavefunctions for quantum-mechanical harmonic oscillators exist in regions beyond the point where classically all energy would be

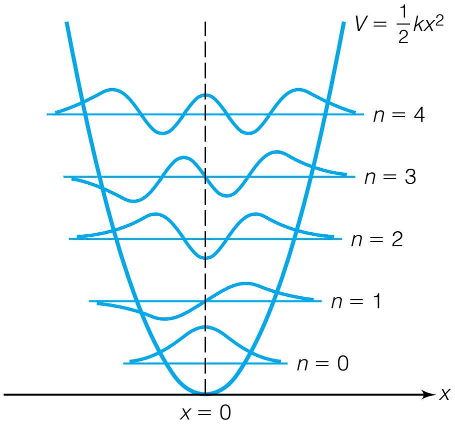


Figure 11.4 Plots of the first five wavefunctions of the harmonic oscillator. They are superimposed against the potential energy for the system. The positions where the wavefunctions go outside the potential energy are called the classical turning points. Classically, a harmonic oscillator will never go beyond its turning point, since it does not have enough energy. Quantum mechanically, there is a nonzero probability that a particle acting as a harmonic oscillator will exist beyond this point.

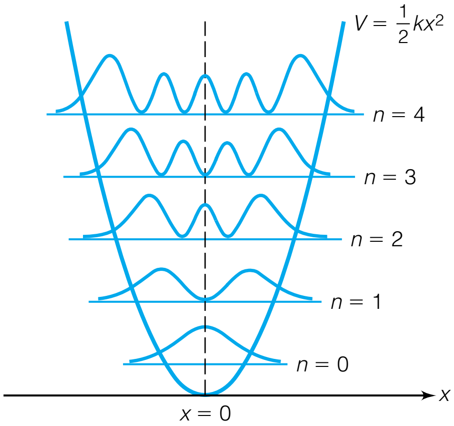


Figure 11.5 Plots of the first five $|\Psi|^2$ wavefunctions, superimposed on the potential energy diagram. As the quantum number increases, the probability that the particle is in the center of the potential energy well decreases and the probability of its being at the sides of the potential well increases. At high quantum numbers, quantum mechanics is mimicking classical mechanics. This is another example of the correspondence principle.

potential energy. That is, wavefunctions are nonzero and therefore the oscillator can exist *beyond* its classical turning point. This suggests the paradoxical conclusion that the oscillator must have negative kinetic energy! Actually, the "paradox" aspect is based on classical expectations. This is not the first example of quantum mechanics proposing something that goes against classical expectations. Tunneling of a particle through a finite barrier is another, and the wavefunction's existence beyond the classical turning point is similar to tunneling. In this case, the "wall" is a curved potential energy surface, not a straight up-and-down barrier.

Recall that the particle's probability of existing anywhere along its one-dimensional space is proportional to $|\Psi|^2$. Several plots of $|\Psi|^2$ are shown in Figure 11.5. The top plot has a high quantum number, and its shape is starting to mimic the behavior of a classical harmonic oscillator: it moves very quickly near $x = 0$ (and has a lower probability of existence there), but pauses near the turning point and has a higher probability of being found there. This is another example of the correspondence principle: for high quantum numbers (and therefore high energies), quantum mechanics approaches the expectations of classical mechanics.

Example 11.7

Evaluate the average value of the momentum (in the x direction) for Ψ_1 of a harmonic oscillator.

Solution

Using the definition of the momentum operator, we need to evaluate

$$\langle p_x \rangle = N^2 \int_{-\infty}^{+\infty} [H_1(\alpha^{1/2}x) \cdot e^{-\alpha x^2/2}]^* \cdot -i\hbar \frac{\partial}{\partial x}[H_1(\alpha^{1/2}x) \cdot e^{-\alpha x^2/2})]\, dx$$

It would be easier to simply use the form of the Hermite polynomial in terms of $\alpha^{1/2}x$ instead of ξ (although it can be done either way; use your judgment regarding which you prefer). From Table 11.1:

$$\langle p_x \rangle = N^2 \int_{-\infty}^{+\infty} (2\alpha^{1/2}x \cdot e^{-\alpha x^2/2})^* \cdot -i\hbar \frac{\partial}{\partial x}(2\alpha^{1/2}x \cdot e^{-\alpha x^2/2})\, dx$$

The complex conjugate does not change anything. Evaluating the derivative in the right-hand part of the expression, and bringing the constants outside the integral:

$$\langle p_x \rangle = -4\alpha i\hbar N^2 \int_{-\infty}^{+\infty} x \cdot e^{-\alpha x^2/2} \cdot (e^{-\alpha x^2/2} - \alpha x^2 e^{-\alpha x^2/2})\, dx$$

which simplifies to

$$\langle p_x \rangle = -4\alpha i\hbar N^2 \int_{-\infty}^{+\infty} (xe^{-\alpha x^2} - \alpha x^3 e^{-\alpha x^2})\, dx$$

Both terms inside the parentheses are odd over the range of integration, overall. Therefore, their integrals are exactly zero. So

$$\langle p_x \rangle = 0$$

Given that momentum is a vector quantity and that the mass is traveling back and forth in both directions, it should make sense that the average value of the momentum is zero.

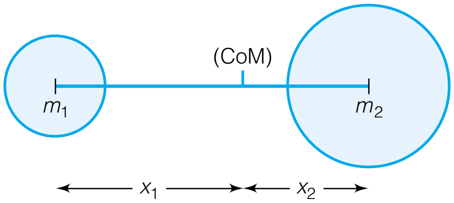


Figure 11.6 Two masses, m_1 and m_2, are moving back and forth with respect to each other with the center of mass (CoM) unmoving. This circumstance is used to define the reduced mass μ.

11.5 The Reduced Mass

Many harmonic oscillators are not simply a single mass moving back and forth, like a pendulum or an atom attached to a massive, unmoving wall. Many are like diatomic molecules, with two atoms each moving back and forth together as in Figure 11.6. But to describe such a system as a harmonic oscillator, the mass of the oscillator isn't the sum of the two masses of the atoms. Such a system needs to be defined a little differently.

We will assume that the two masses m_1 and m_2 in Figure 11.6 have positions labeled as x_1 and x_2 but are moving back and forth as a harmonic oscillator. We will ignore any other motion of these two masses (like translation or rotation) and focus solely on the oscillation. In a purely harmonic oscillation (also called a *vibration*), the center of mass* does not change, so that

$$m_1\frac{dx_1}{dt} = -m_2\frac{dx_2}{dt}$$

The negative sign indicates that the masses are moving in the opposite directions. By adding the mixed term $m_2(dx_1/dt)$ to both sides, we get

$$m_1\frac{dx_1}{dt} + m_2\frac{dx_1}{dt} = -m_2\frac{dx_2}{dt} + m_2\frac{dx_1}{dt}$$

$$(m_1 + m_2)\frac{dx_1}{dt} = m_2\left(\frac{dx_1}{dt} - \frac{dx_2}{dt}\right)$$

(where on the right side we have switched the order of the derivatives). This is rearranged to

$$\frac{dx_1}{dt} = \frac{m_2}{m_1 + m_2}\left(\frac{dx_1}{dt} - \frac{dx_2}{dt}\right) \tag{11.20}$$

It is very convenient in many cases to define *relative* coordinates instead of absolute coordinates. For example, specifying certain values of Cartesian coordinates is a way of using absolute coordinates. However, *differences* in Cartesian coordinates are relative, because the difference doesn't depend on the starting and ending values (for example, the difference between 5 and 10 is the same as the difference between 125 and 130). If we define the relative coordinate q as

$$q \equiv x_1 - x_2$$

and thus

$$\frac{dq}{dt} \equiv \frac{dx_1}{dt} - \frac{dx_2}{dt}$$

Now we can substitute into equation 11.20 to get

$$\dot{x}_1 = \frac{dx_1}{dt} = \frac{m_2}{m_1 + m_2}\frac{dq}{dt} \tag{11.21}$$

where we use $\dot{x}_1$ to indicate the time derivative of x. By performing a parallel addition of $m_1\ dx_2/dt$ to the original center-of-mass expression, we can also get

$$\dot{x}_2 = \frac{dx_2}{dt} = \frac{m_1}{m_1 + m_2}\frac{dq}{dt} \tag{11.22}$$

as a second expression.

---

*Recall that the center of mass $(x_{\text{cm}}, y_{\text{cm}}, z_{\text{cm}})$ of a multiparticle system is defined as $x_{\text{cm}} = (\Sigma m_i \cdot x_i)/(\Sigma m_i)$, where each sum is over the i particles in the system, m_i is the particle's mass, and x_i is the particle's x coordinate; and similar expressions apply for y_{cm} and z_{cm}.

In considering the total energy of this harmonic oscillation, the potential energy is the same as for any other harmonic oscillator but the kinetic energy is the sum of the kinetic energies of the two particles. That is,

$$K = \tfrac{1}{2}m_1\dot{x}_1^2 + \tfrac{1}{2}m_2\dot{x}_2^2$$

Using equations 11.21 and 11.22, it is easy to substitute and show that the kinetic energy has a simple form in terms of the time derivative of the relative coordinate $\dot{q}$:

$$K = \frac{1}{2}\frac{m_1 m_2}{m_1 + m_2}\dot{q}^2 \qquad \textbf{(11.23)}$$

The *reduced mass* μ is defined as

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2} \qquad \textbf{(11.24)}$$

so that the total kinetic energy is simply

$$\mathrm{K} = \tfrac{1}{2}\mu\dot{q}^2 \qquad \textbf{(11.25)}$$

which is a simpler expression for the kinetic energy. The reduced mass can also be determined using the expression

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \qquad \textbf{(11.26)}$$

What this means is that the kinetic energy of the oscillator can be represented by the kinetic energy of *a single mass moving back and forth,* if that single mass has the reduced mass of the two masses in the original system. This allows us to treat the *two*-particle harmonic oscillator as a one-particle harmonic oscillator and use the same equations and expressions that we derived for a simple harmonic oscillator. So all of the equations of the previous sections apply, assuming one uses the *reduced* mass of the system. For example, equation 11.3 becomes

$$\nu = \frac{1}{\tau} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \textbf{(11.27)}$$

The Schrödinger equation, in terms of the reduced mass, is

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \hat{V}(x)\right]\Psi = E\Psi \qquad \textbf{(11.28)}$$

Fortunately, our derivations need not be repeated because we can simply substitute μ for m in any affected expression. The unit of reduced mass is mass, as is easily shown.

Example 11.8

Show that reduced mass has units of mass.

Solution

Substituting just units into equation 11.24, we get

$$\mu = \frac{\mathrm{kg}\cdot\mathrm{kg}}{\mathrm{kg} + \mathrm{kg}} = \frac{\mathrm{kg}^2}{\mathrm{kg}} = \mathrm{kg}$$

which confirms that the reduced mass has units of mass.

Example 11.9

The hydrogen molecule vibrates at a frequency of about 1.32×10^{14} Hz. Calculate the following:

a. The force constant of the H–H bond

b. The change in energy that accompanies a transition from the $n = 1$ to $n = 2$ vibrational level, assuming that the hydrogen molecule is acting as an ideal harmonic oscillator

Solution

a. The mass of a single hydrogen atom, in kilograms, is 1.674×10^{-27} kg. Therefore, the reduced mass of a hydrogen molecule is

$$\mu = \frac{(1.674 \times 10^{-27}\ \text{kg})(1.674 \times 10^{-27}\ \text{kg})}{1.674 \times 10^{-27}\ \text{kg} + 1.674 \times 10^{-27}\ \text{kg}} = 8.370 \times 10^{-28}\ \text{kg}$$

Using the rearranged equation 11.5 in terms of k and remembering to use the reduced mass in place of the mass, we find

$$k = 4\pi^2(1.32 \times 10^{14}\ \text{s}^{-1})^2(8.370 \times 10^{-28}\ \text{kg})$$

$$k = 575\ \text{kg/s}^2$$

which, as explained earlier, is equal to 575 N/m or 5.75 mdyn/Å.

b. According to equation 11.16, the energy of a harmonic oscillator is

$$E = (n + \tfrac{1}{2})h\nu$$

For $n = 1$ and 2, the energies are

$$E(n = 1) = (1 + \tfrac{1}{2})(6.626 \times 10^{-34}\ \text{J·s})(1.32 \times 10^{14}\ \text{s}^{-1}) = 1.31 \times 10^{-19}\ \text{J}$$

$$E(n = 2) = (2 + \tfrac{1}{2})(6.626 \times 10^{-34}\ \text{J·s})(1.32 \times 10^{14}\ \text{s}^{-1}) = 2.19 \times 10^{-19}\ \text{J}$$

The difference in energy is 2.19×10^{-19} J minus 1.31×10^{-19} J, or 8.8×10^{-20} J.

Example 11.10

The HF molecule has a harmonic vibrational frequency of 1.241×10^{14} Hz.

a. Determine its force constant using the reduced mass of HF.

b. Assume that the F atom doesn't move and that the vibration is due solely to the motion of the H atom. Using the mass of the H atom and the force constant just calculated, what is the expected frequency of the atom? Comment on the difference.

Solution

a. Using the masses of H and F as 1.674×10^{-27} kg and 3.154×10^{-26} kg respectively, the reduced mass can be calculated as

$$\mu = \frac{(1.674 \times 10^{-27}\ \text{kg})(3.154 \times 10^{-26}\ \text{kg})}{1.674 \times 10^{-27}\ \text{kg} + 3.154 \times 10^{-26}\ \text{kg}} = 1.590 \times 10^{-27}\ \text{kg}$$

Substituting into the same expression as in the previous example, we find for k:

$$k = 4\pi^2(1.241 \times 10^{14}\ \text{s}^{-1})^2(1.590 \times 10^{-27}\ \text{kg}) = 966.7\ \text{kg/s}^2$$

b. The vibrational frequency expected for a hydrogen atom having a mass of 1.674×10^{-27} kg and a vibrational force constant of 967 kg/s^2 is given by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{966.7\ \text{kg/s}^2}{1.674 \times 10^{-27}\ \text{kg}}}$$

$$\nu = 1.209 \times 10^{14}\ \text{Hz}$$

This is a somewhat lower frequency, about $2\frac{1}{2}\%$ lower, than is found experimentally. This illustrates that using the reduced mass does have an effect on the calculation. The effect is even more obvious when the two particles have similar masses. Repeat this example using H_2 (see example 11.9) and HD, where D = ^{2}H.

In all cases where multiple particles are moving *relative* to each other in our system, the reduced mass must be considered in place of the actual mass. In the harmonic oscillator, two particles are moving relative to each other, and so the reduced mass is used. In a purely translational motion, two masses are moving through space but remain in the same positions *relative to each other.* Therefore, the sum of the masses, the total mass, is the correct mass needed to describe the translational motion.

11.6 Two-Dimensional Rotations

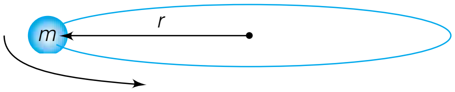


Figure 11.7 Two-dimensional rotational motion can be defined as a mass moving about a point in a circle with fixed radius *r*.

Another model system consists of a mass traveling in a circle. A simplistic diagram of such a system is shown in Figure 11.7. The particle having mass m is moving in a circle having a *fixed* radius r. There may or may not be another mass at the center, but the only motion under consideration is that of the particle at radius r. For this system the potential energy V is fixed and can be arbitrarily set to 0. Since the particle is moving in two dimensions, chosen as the x and y dimensions, the Schrödinger equation for this system is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\Psi = E\Psi \qquad \textbf{(11.29)}$$

This is actually not the best form for the Schrödinger equation. Since the particle is moving at a fixed radius and changing only its angle as it moves in a circle, it makes sense to try and describe the motion of the particle in terms of its angular motion, not its Cartesian motion. Otherwise, we would have to be able to solve the above Schrödinger equation in two dimensions simultaneously. Unlike the 3-D particle-in-a-box, we cannot separate the x motion from the y motion in this case, since our particle is moving in both x and y dimensions simultaneously.

To find eigenfunctions for the Schrödinger equation, it will be easier if we express the total kinetic energy in terms of angular motion. Classical mechanics states that a particle moving in a circle has *angular momentum,* which was defined in Chapter 9 as $L = mvr$. However, we can also define angular momentum in terms of linear momenta, p_i, in each dimension. If a particle is confined to the xy plane, then it has angular momentum along the z axis whose magnitude is given by the classical mechanics expression

$$L_z = xp_y - yp_x \qquad \textbf{(11.30)}$$

where p_x and p_y are the linear momenta in the x and y directions. At this time, we are ignoring the vector property of the momenta (except for its z direction) for the sake of simplicity.

In terms of the angular momentum, the kinetic energy of a particle having mass m and revolving at a distance r about a center is

$$K = \frac{L_z^2}{2mr^2} = \frac{L_z^2}{2I} \tag{11.31}$$

where I has been defined as mr^2 and is called the *moment of inertia*. (You should be aware that there are different expressions for the moment of inertia of a physical object depending on the shape of the object. The expression $I = mr^2$ is the moment of inertia for a single mass moving in a circular path.)

Quantum mechanically, since operators for linear momenta are defined, an operator for the angular momentum can also be defined:

$$\hat{L}_z = -i\hbar\left(\hat{x}\frac{\partial}{\partial y} - \hat{y}\frac{\partial}{\partial x}\right) \tag{11.32}$$

By analogy, therefore, one can write the Schrödinger equation for this system in terms of equations 11.31 and 11.32 as

$$\frac{\hat{L}_z^{\,2}}{2I}\Psi = E\Psi \tag{11.33}$$

As useful as the angular operator will be, it is still not in its best form, since using it in the Hamiltonian will still lead to an expression in terms of x and y. Instead of using Cartesian coordinates to describe the circular motion, we will use polar coordinates. In *polar coordinates,* the entire two-dimensional space can be described using a radius from the center, r, and an angle ϕ measured from some specified direction (typically the positive x axis). Figure 11.8 shows how the polar coordinates are defined. In polar coordinates, the angular momentum operator has a very simple form:

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi} \tag{11.34}$$

By using this form of the angular momentum, the Schrödinger equation for two-dimensional rotation becomes

$$-\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2}\Psi = E\Psi \tag{11.35}$$

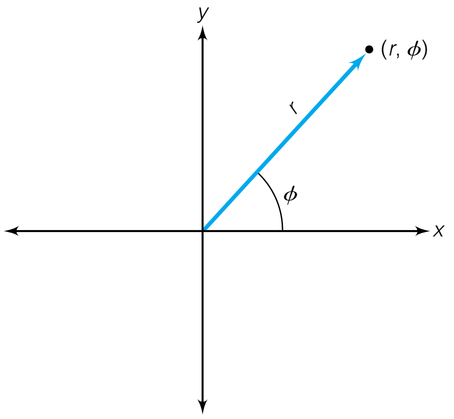


Figure 11.8 Two-dimensional polar coordinates are defined as a distance from an origin, r, and an angle ϕ with respect to some arbitrary direction. Here, ϕ is the angle made with the positive x axis.

Equation 11.35 shows that even though we call this system "two-dimensional motion," in polar coordinates only one coordinate is changing: the angle ϕ. Equation 11.35 is a simple second-order differential equation that has known analytic solutions for Ψ, which is what we are trying to find. The possible expressions for Ψ are

$$\Psi = Ae^{im\phi} \tag{11.36}$$

where the values of the constants A and m will be determined shortly, ϕ is the polar coordinate introduced above, and i is the square root of -1. (Do not confuse the constant m with the mass of a particle.) The astute reader will recognize that this wavefunction can be written in terms of ($\cos m\phi + i \sin m\phi$), but the exponential expression above is the more useful form.

Although the wavefunction above satisfies the Schrödinger equation, proper wavefunctions must also have other properties. First, they must be bounded.

This is not a problem (as inspection of the cosine/sine form of the wavefunction shows). They must be continuous and differentiable. Again, exponential functions of this sort are mathematically well behaved.

They must also be single-valued, and this presents a potential problem. Because the particle is traveling in a circle, it retraces its path after 360° or 2π radians. When it does so, the ''single-valued" condition of acceptable wavefunctions requires that the value of the wavefunction be the same when the particle makes a complete circle. (This is also sometimes called a circular boundary condition.) Mathematically, this is written as

$$\Psi(\phi) = \Psi(\phi + 2\pi)$$

We can use the form of the wavefunction in equation 11.36 and simplify in steps:

$$Ae^{im\phi} = Ae^{im(\phi+2\pi)}$$
$$e^{im\phi} = e^{im\phi}e^{\mathrm{im}2\pi}$$
$$1 = e^{2\pi im}$$

where A and $\mathrm{e}^{im\phi}$ have been canceled out sequentially in each step, and in the last step the symbols in the exponent have been rearranged. This last equation is the key. It is probably better followed if we use *Euler's theorem* ($e^{i\theta} = \cos\theta + i\sin\theta$) and write the imaginary exponential in terms of sine and cosine:

$$e^{2\pi im} = \cos 2\pi m + i\sin 2\pi m = 1$$

In order for this equation to be satisfied, the sine term must be exactly zero (because the number 1 has no imaginary part to it) and the cosine term must be exactly 1. This will occur only when $2\pi m$ is equal to any multiple of 2π (including 0 and negative values):

$$2\pi m = 0, \pm 2\pi, \pm 4\pi, \pm 6\pi, \ldots$$

This means that the number m must have only whole number values:

$$m = 0, \pm 1, \pm 2, \pm 3, \ldots$$

Thus, the constant m in the exponential cannot be any arbitrary constant, but it must be an *integer* in order to have a properly behaved wavefunction. Therefore the wavefunctions are not just arbitrary exponential functions, but a set of exponential functions where the exponents must have certain specified values. The number m is a *quantum number.*

In order to normalize the wavefunction, we need to determine $d\tau$ and the limits of the integral. Since the only thing changing is ϕ, the infinitesimal for integration is simply $d\phi$. The value of ϕ goes from 0 to 2π before it starts to repeat the space it is covering, so the limits of integration are 0 to 2π. The normalization of the wavefunction proceeds as follows.

$$N^2 \int_0^{2\pi} (e^{im\phi})^* e^{im\phi}\, d\phi = 1$$

For the first time in these model systems, the complex conjugate changes something in the wavefunction: it affects i in the exponent of the function. The first exponent becomes negative:

$$N^2 \int_0^{2\pi} e^{-im\phi} e^{im\phi}\, d\phi = 1$$

The two exponential functions cancel each other out, leaving only the infinitesimal. The normalization is completed:

$$N^2 \int_0^{2\pi} d\phi = 1$$

$$N^2 \phi\big|_0^{2\pi} = 1$$

$$N^2(2\pi) = 1$$

$$N^2 = \frac{1}{2\pi}$$

$$N = \frac{1}{\sqrt{2\pi}}$$

where again only the positive square root is used. The complete wavefunction for two-dimensional rotational motion, then, is:

$$\Psi_m = \frac{1}{\sqrt{2\pi}} e^{im\phi} \qquad m = 0, \pm 1, \pm 2, \pm 3, \ldots \tag{11.37}$$

The normalization constant is the same for all wavefunctions and does not depend on the quantum number m. Figure 11.9 shows plots of the first few Ψ's. The magnitudes of the Ψ's are reminiscent of circular standing waves, and these are also suggestive of de Broglie's picture of electrons in a circular orbital. It is only suggestive, and this analogy is not meant to hint that this is a true description of electron motion.

Now the energy eigenvalues of the system can be evaluated. It is given by the Schrödinger equation, of course:

$$-\frac{\hbar^2}{2I}\frac{\partial^2}{\partial \phi^2}\Psi = E\Psi$$

By inserting the general form of the wavefunction given in equation 11.37, we get

$$\frac{-\hbar^2}{2I}\frac{\partial^2}{\partial \phi^2}\left(\frac{1}{\sqrt{2\pi}}e^{im\phi}\right) = E\left(\frac{1}{\sqrt{2\pi}}e^{im\phi}\right)$$

The second derivative of the exponential is easily evaluated as $-m^2 e^{im\phi}$. (The constant $1/\sqrt{2\pi}$ is not affected by the derivative.) Substituting and rearranging the constants to keep the terms in the original wavefunction grouped together:

$$\frac{m^2\hbar^2}{2I}\left(\frac{1}{\sqrt{2\pi}}e^{im\phi}\right) = E\left(\frac{1}{\sqrt{2\pi}}e^{im\phi}\right)$$

This shows that the eigenvalue is $m^2\hbar^2/2I$. Since the eigenvalue of the Schrödinger equation corresponds to the energy observable, the conclusion is that

$$E = \frac{m^2\hbar^2}{2I} \tag{11.38}$$

where $m = 0, \pm 1, \pm 2$, etc. A certain specified mass at a fixed distance r has a certain moment of inertia I. Planck's constant is a constant, so the only variable in the expression for energy is an integer m. Therefore, *the total energy of a rotating particle is quantized* and depends on the quantum number m. The following example shows how these quantities come together to yield units of energy.

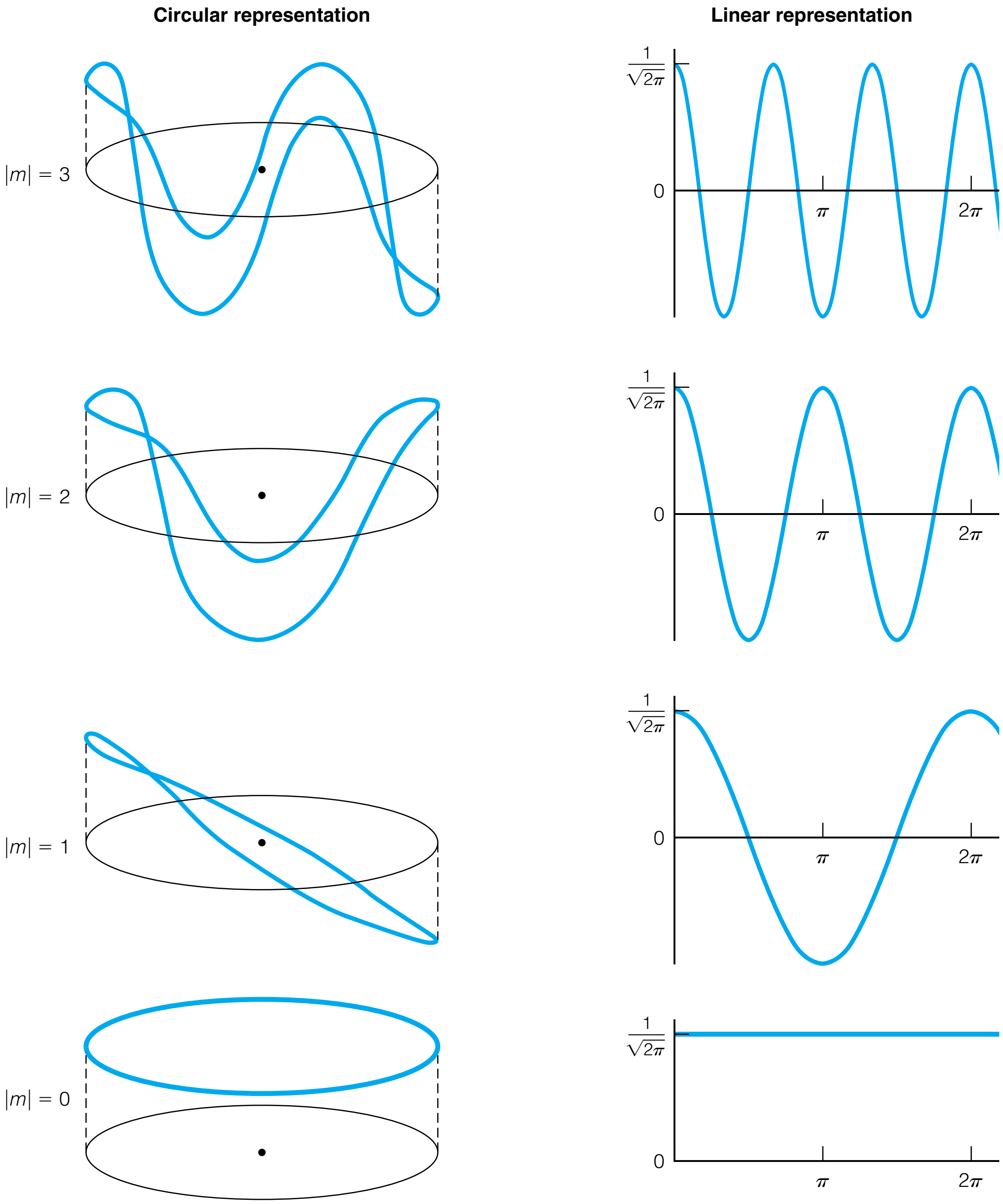


Figure 11.9 The first four 2-D rotational wavefunctions. The circular representations mimic the true geometry of the system, and the linear representations clarify what the wavefunctions look like. Each linear representation represents one circuit (2π radians) of the rigid rotor.

Example 11.11

An electron is traveling in a circle having radius 1.00 Å. Calculate the energy eigenvalues of the first five 2-D rotational wavefunctions; that is, where $m = 0, \pm 1$, and ± 2.

Solution

First, we calculate the moment of inertia of the electron. Using $m_e = 9.109 \times 10^{-31}$ kg and the given radius of 1.00 Å $= 1.00 \times 10^{-10}$ m, the moment of inertia is

$$I = mr^2 = (9.109 \times 10^{-31}\ \text{kg})(1.00 \times 10^{-10}\ \text{m})^2 = 9.11 \times 10^{-51}\ \text{kg·m}^2$$

These are the correct units for the moment of inertia. Now we can consider the energies of each state. Since $m = 0$ for the first state, it is easy to see that

$$E(m = 0) = 0$$

For the other states, we recall that the energy is dependent on the square of the quantum number. Therefore, the energy when $m = 1$ is the same as the energy when $m = -1$.

$$E(m = \pm 1) = \frac{1^2(6.626 \times 10^{-34}\ \text{J·s})^2}{2(9.11 \times 10^{-51}\ \text{kg·m}^2)(2\pi)^2} = 6.10 \times 10^{-19}\ \text{J}$$

$$E(m = \pm 2) = \frac{2^2(6.626 \times 10^{-34}\ \text{J·s})^2}{2(9.11 \times 10^{-51}\ \text{kg·m}^2)(2\pi)^2} = 2.44 \times 10^{-18}\ \text{J}$$

The $(2\pi)^2$ terms in the denominators are on account of $\hbar$. The units come out to joules, which the following unit analysis illustrates:

$$\frac{(\text{J·s})^2}{\text{kg·m}^2} = \frac{\text{J}^2\text{·s}^2}{\text{kg·m}^2} = \frac{\text{J·s}^2}{\text{kg·m}^2}\left(\frac{\text{kg·m}^2}{\text{s}^2}\right) = \text{J}$$

where in the next-to-last step, one of the joule units is broken down into its basic units.

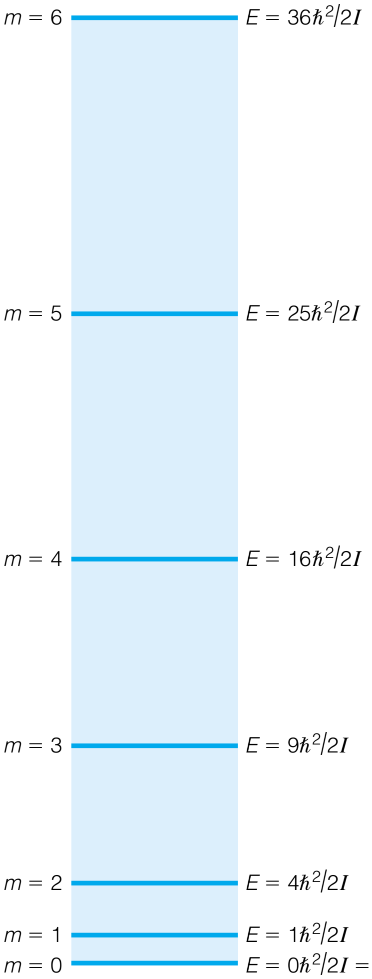


Figure 11.10 The quantized energy levels of 2-D rotation. They increase in energy according to the *square* of the quantum number *m*.

A diagram of the energy levels of two-dimensional rotational motion is given in Figure 11.10. As for the particle-in-a-box, the energy depends on the square of the quantum number, instead of changing linearly with the quantum number. The energy levels get spaced farther apart as the quantum number m gets larger.

Because of the square dependence of the energy on the quantum number m, negative values of m yield the same value of energy as do the positive values of the same magnitude (as noted in Example 11.11). Therefore, all energy levels (except for the $m = 0$ state) are *doubly degenerate:* two wavefunctions have the same energy.

This system has one more observable to consider: the angular momentum, in terms of which the total energy was defined. If the wavefunctions are eigenfunctions of the angular momentum operator, the eigenvalue produced would correspond to the observable of the angular momentum. Using the polar-coordinate form of the angular momentum operator:

$$\hat{L}_z\Psi = -i\hbar\frac{\partial}{\partial\phi}\left(\frac{1}{\sqrt{2\pi}}e^{im\phi}\right) = -i\hbar(im)\left(\frac{1}{\sqrt{2\pi}}e^{im\phi}\right)$$

$$\hat{L}_z\Psi = m\hbar\Psi \tag{11.39}$$

The wavefunctions that are eigenfunctions of the Schrödinger equation are also eigenfunctions of the angular momentum operator. Consider the eigenvalues themselves: a product of $\hbar$, a constant, and the quantum number m. *The angular momentum of the particle is quantized.* It can have only certain values, and those values are dictated by the quantum number m.

Example 11.12

What are the angular momenta of the five states of the rotating electron from Example 11.11?

Solution

According to equation 11.39, the values of the angular momenta are $-2\hbar$, $-1\hbar$, 0, $1\hbar$, and $2\hbar$. Notice that although the energies are the same for certain pairs of quantum numbers, the values of the quantized angular momenta are not.

A few comments are necessary about the angular momentum. First, classical mechanics treats possible angular momentum values as continuous, whereas quantum mechanics limits angular momentum to discrete, quantized values. Second, the quantized angular momentum does not depend on mass or moment of inertia. This is completely counter to the ideas of classical mechanics, where the mass of a particle is intimately tied to its momentum. This is another example in which quantum mechanics departs from the ideas of classical mechanics.

Also, because the quantized values of angular momentum depend on m and not m^2, every wavefunction has its own characteristic value of the angular momentum, as mentioned in Example 11.12. The energy levels may be doubly degenerate, but each state has its own angular momentum. One state has an angular momentum value of $m\hbar$, and the other $-m\hbar$. Since momentum is a vector quantity, there is a simple way of rationalizing the differences between the two states. In one state, the particle is moving in one direction (say, clockwise), and in the other, it is moving in the opposite direction (say, counterclockwise).

In cases where two masses (say, two atoms) are connected and rotating in a plane, all of the above equations would apply except that the mass would be replaced by the *reduced mass* of the two-mass system. This is consistent with earlier treatments of two masses moving relative to each other. A system of two (or more) particles rotating in two dimensions is called a *2-D rigid rotor*.

Example 11.13

The bond distance in HCl is 1.29 Å. In its lowest rotational state, the molecule is not rotating, and so the rigid rotor equations indicate that its rotational energy is zero. What are its energy and its angular momentum when it is in the first nonzero energy state? Use the atomic weight of Cl as an approximation for the mass of the Cl atom.

Solution

Using the masses of H and Cl as 1.674×10^{-27} kg and 5.886×10^{-26} kg, the reduced mass of the molecule is 1.628×10^{-27} kg. The bond distance, in units of meters, is 1.29×10^{-10} m. For this case we will not calculate the moment of inertia as a separate step, but will substitute the numbers into the energy formula as appropriate. For the first nonzero rotational energy state:

$$E(m = 1) = \frac{(1)^2(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})^2}{2(1.628 \times 10^{-27}\ \text{kg})(1.29 \times 10^{-10}\ \text{m})^2(2\pi)^2}$$

$$E(m = 1) = 2.05 \times 10^{-22}\ \text{J}$$

Because the molecule can have this energy in the $m = 1$ state and the $m = -1$ state, the angular momentum of the molecule can be either $1\hbar$ or $-1\hbar$. With the information provided, there is no way to distinguish between the possibilities.

Planck's constant h has the same units, J·s, as the angular momentum, kg·m^2/s. This is a different unit from that of *linear* momentum, where the unit is kg·m/s. Planck's constant h has units that classical mechanics would call units of *action*. What we will find is that any atomic observable that has units of action is an angular momentum of a sort, and its value at the atomic level is related to Planck's constant. It is relationships like this that reinforce the central, irreplaceable role of Planck's constant in the understanding (indeed, the very existence) of matter.

Finally, now that we have shown that angular momentum is quantized for some systems, we bring up an old idea, one that Bohr had when he put forth his theory of the hydrogen atom. He assumed that the angular momentum was quantized! By doing so, Bohr was able to theoretically predict the hydrogen atom spectrum, although the justification of the assumption was highly debatable. Quantum mechanics does not assume the quantization of angular momentum. Rather, quantum mechanics shows that it is inevitable.

Example 11.14

The organic molecule benzene, C_6H_6, has a cyclic structure where the carbon atoms make a hexagon. The π electrons in the cyclic molecule can be approximated as having two-dimensional rotational motion. Calculate the diameter of this "electron ring" if it is assumed that a transition occurring at 260.0 nm corresponds to an electron going from $m = 3$ to $m = 4$.

Solution

First, calculate the energy change in J that corresponds to a photon wavelength of 260.0 nm, which is 2.60×10^{-7} m:

$$c = \lambda\nu$$

$$2.9979 \times 10^{8}\ \text{m/s} = (2.60 \times 10^{-7}\ \text{m}) \cdot \nu$$

$$\nu = 1.15 \times 10^{15}\ \text{s}^{-1}$$

Therefore, using $E = h\nu$:

$$E = (6.626 \times 10^{-34}\ \text{J·s})(1.15 \times 10^{15}\ \text{s}^{-1})$$

$$E = 7.64 \times 10^{-19}\ \text{J}$$

This energy difference should be equal to the energy difference between the $m = 4$ and $m = 3$ energy levels:

$$\Delta E = 7.64 \times 10^{-19}\ \text{J} = \frac{4^2\hbar^2}{2mr^2} - \frac{3^2\hbar^2}{2mr^2}$$

where mr^2 has been substituted for I in the denominators. Substituting for h, 2π, and the mass of the electron:

$$7.64 \times 10^{-19}\ \text{J}$$
$$= \frac{4^2(6.626 \times 10^{-34}\ \text{J·s})^2}{(2\pi)^2 \cdot 2(9.109 \times 10^{-31}\ \text{kg}) \cdot r^2} - \frac{3^2(6.626 \times 10^{-34}\ \text{J·s})^2}{(2\pi)^2 \cdot 2(9.109 \times 10^{-31}\ \text{kg}) \cdot r^2}$$

$$7.64 \times 10^{-19}\ \text{J} = (16 - 9)\frac{6.104 \times 10^{-39}\ \text{m}^2}{r^2}$$

$$r^2 = 5.59 \times 10^{-20}\ \text{m}^2$$

$$r = 2.36 \times 10^{-10}\ \text{m} = 2.36\ \text{Å}$$

The benzene molecule has a *diameter* of a little over 3 Å across. The "electron ring" is assumed to be slightly less than that, on average. This model predicts a slightly larger diameter (= 2 radii, or ~4.7 Å in this case) than is the case. However, given the approximations that were part of our assumptions in applying this model to benzene, getting this close should be taken as a positive sign.

Two-dimensional rotational motion is the last system we consider where the solution of the wavefunction is derived. Henceforth, major conclusions will be presented instead of being derived explicitly. The systems considered to this point have demonstrated sufficiently how the postulates of quantum mechanics are applied to systems and how the results are obtained. After this, we will concentrate more on the results and what they mean, rather than a step-by-step derivation of the solutions. If you are interested in the mathematical details, consult a more advanced reference.

11.7 Three-Dimensional Rotations

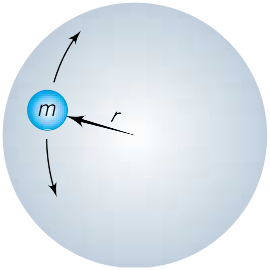


Figure 11.11 Three-dimensional rotations can be defined as a mass moving along the surface of a sphere having fixed radius *r*.

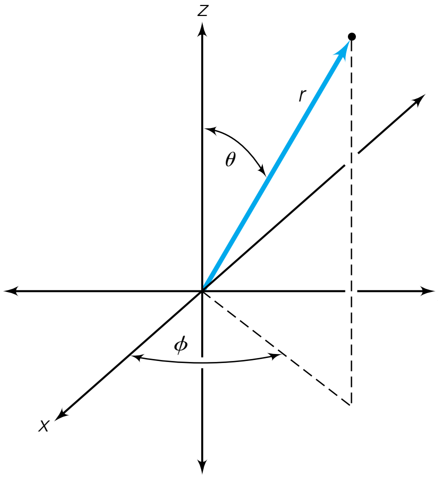


Figure 11.12 The definitions of spherical polar coordinates *r*, θ, and ϕ. The coordinate *r* is the distance between a point and the origin. The angle ϕ is defined with respect to the projection of the *r* vector in the *xy* plane, and is the angle that this projection makes with the positive *x* axis (motion toward the positive *y* axis being considered a positive angular value). The angle θ is the angle between the *r* vector and the positive *z* axis.

It is a trivial step to expand rotation of a particle or rigid rotor to three dimensions. The radius of a particle from a center is still fixed, so three-dimensional rotation describes motion on the surface of a sphere, as shown in Figure 11.11. However, in order to be able to describe the complete sphere, the coordinate system is expanded to include a second angle θ. Together, the three coordinates (r, θ, ϕ) define *spherical polar coordinates.* The definitions of these coordinates are shown in Figure 11.12. In order to treat the subject at hand more efficiently, several statements regarding spherical polar coordinates are presented without proof (although they can be proven without much effort, if desired).

There is a straightforward relationship between three-dimensional Cartesian coordinates (x, y, z) and spherical polar coordinates (r, θ, ϕ). They are

$$\begin{aligned} x &= r \sin\theta \cos\phi \\ y &= r \sin\theta \sin\phi \\ z &= r \cos\theta \end{aligned} \tag{11.40}$$

When one performs integrations in spherical polar coordinates, the form of $d\tau$ and the limits of integration must be considered. The full form of $d\tau$ for integration over all three coordinates (which would be a triple integral, each integral dealing independently with a single polar coordinate) is

$$d\tau = r^2 \sin\theta \, dr \, d\phi \, d\theta \tag{11.41}$$

In the case of 2-D integration over only ϕ and θ, the infinitesimal $d\tau$ is

$$d\tau = \sin\theta \, d\phi \, d\theta \tag{11.42}$$

Because two angles are defined, in order to integrate over all space just once, one angle's integration limits go from 0 to π while the other angle's integration limits range from 0 to 2π (if both limits were 0 to 2π, one would end up covering all space twice). The accepted convention is that the integration limits on ϕ are from 0 to 2π, and the limits on θ go from 0 to π. In cases where integration in terms of r is considered, the integration limits are 0 to ∞.

Finally, as in the case of the 2-D rotational motion, the form of the Hamiltonian is different when using spherical polar coordinates. In the case where θ and ϕ are varied (but r is still constant!), the Hamiltonian operator is

$$\widehat{H} = -\frac{\hbar^2}{2I}\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) + \widehat{V} \tag{11.43}$$

where I is the moment of inertia and $\widehat{V}$ is the potential energy operator. As with two-dimensional rotations, the Hamiltonian can be written in terms of the angular momentum, but now it must be written in terms of the *total* angular momentum, not just in terms of the angular momentum in a single dimension. The 3-D rotational Hamiltonian is thus also written as

$$\widehat{H} = \frac{\widehat{L}^2}{2I} + \widehat{V} \tag{11.44}$$

By inspecting the two previous expressions, you can see that

$$\widehat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) \tag{11.45}$$

The square root of the right side of equation 11.45 *cannot be taken analytically.* Therefore, an operator for the total angular momentum is not commonly used in 3-D quantum mechanical systems. Only an operator for the *square* of the total angular momentum is common. In order to find the angular momentum, one must determine the value (ultimately an eigenvalue) of the square of the angular momentum, then take the square root of that observable.

Again, the potential energy V for 3-D rotational motion can be set to zero, so acceptable wavefunctions for rotation in three dimensions must satisfy the Schrödinger equation, which is

$$\frac{-\hbar^2}{2I}\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\Psi = E\Psi \tag{11.46}$$

Even though the mass is moving in all three Cartesian coordinates, in spherical polar coordinates we only need θ and ϕ to define the motion. The detailed solution of the above differential equation is long, and will not be presented here. However, several points can be made before the solution is simply presented. First, it is assumed that the solution is *separable.* That is, we assume that the wavefunctions are products of two functions Φ and Θ, each of which depends only on the variables ϕ and θ, respectively:

$$\Psi(\phi, \theta) \equiv \Phi(\phi) \cdot \Theta(\theta)$$

If we consider the variables θ and ϕ in equation 11.46 independently, we see that only one term in the differential contains ϕ, the last term. If θ were held constant, then the first two differential terms would be identically zero (derivatives are zero if the variable in question is held constant), and the Schrödinger equation would have the same form as that for 2-D rotational motion. Therefore, the first part of the solution contains only the variable ϕ and is the same function derived for the 2-D rotating system:

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$

The same restrictions on the possible values of m, the quantum number, hold true in this case, also: $m = 0, \pm 1, \pm 2$, and so on.

Unfortunately, a similar analysis cannot be done by holding ϕ constant and varying only θ in order to find the function $\Theta(\theta)$. This is because all three of the

Table 11.3 The associated Legendre polynomials θ_{ℓ,m_ℓ}

ℓ	m_ℓ	$\theta\ell,m_\ell$
0	0	$\frac{1}{2}\sqrt{2}$
1	0	$\frac{1}{2}\sqrt{6}\cos\theta$
1	±1	$\frac{1}{2}\sqrt{3}\sin\theta$
2	0	$\frac{1}{4}\sqrt{10}(\cos^2\theta - 1)$
2	±1	$\frac{1}{2}\sqrt{15}\sin\theta\cos\theta$
2	±2	$\frac{1}{4}\sqrt{15}\sin^2\theta$
3	0	$\frac{3}{4}\sqrt{14}(\frac{5}{3}\cos^3\theta - \cos\theta)$
3	±1	$\frac{1}{8}\sqrt{42}\sin\theta(5\cos^2\theta - 12)$
3	±2	$\frac{1}{4}\sqrt{105}\sin^2\theta\cos\theta$
3	±3	$\frac{1}{8}\sqrt{70}\sin^3\theta$

differential terms in the Hamiltonian contain θ, so no simplification is gained. (The third term is not a differential in terms of θ, but it does have the $\sin^2\theta$ term in the denominator.) The mixing of variables in the third term introduces another twist. The ultimate solution for $\Theta(\theta)$ will also depend on the quantum number m. In addition, we will find that the limitations imposed on the acceptable wavefunctions (that is, they must be bounded) will generate a relationship between the quantum number m and whatever new quantum number arises.

The θ part of the differential in equation 11.46 does have a known solution. The solution is a set of functions known as *associated Legendre polynomials.* (As with the Hermite polynomials, differential equations of the form in equation 11.46 had been previously studied, by the French mathematician Adrien Legendre, but for different reasons.) These polynomials, listed in Table 11.3, are functions of θ only, but have two indices labeling the functions. One of the indices, an integer denoted ℓ, indicates the maximum power, or *order,* of θ terms. (It also indicates the total order of the combination of $\cos\theta$ and $\sin\theta$ terms.) The second index, m, specifies which particular combination of $\sin\theta$ and $\cos\theta$ terms are in the Legendre polynomial of that particular order. For associated Legendre polynomials, the absolute value of m yields the same polynomial. The possible combinations are limited to those where the absolute value of m always has a value less than or equal to ℓ. That is, because of the requirements of the associated Legendre polynomials, there is a new *quantum number* ℓ whose value must be some nonnegative integer:

$$\ell = 0, 1, 2, \ldots \tag{11.47}$$

and the only possible values of the m quantum number associated with any particular quantum number ℓ are those integers whose absolute value is less than or equal to ℓ:

$$|m| \leq \ell \tag{11.48}$$

These constraints are imposed by the forms of the polynomials, which must be *acceptable wavefunctions and eigenfunctions of the Schrödinger equation.* Because of the limit that ℓ puts on m, it is common to use the symbol m_ℓ as the label for this quantum number.

Example 11.15

List the possible values of m_ℓ for the first five possible values of ℓ.

Solution

The quantum number ℓ can have integer values starting from zero. Therefore, the first five possible values of ℓ are 0, 1, 2, 3, and 4. For $\ell = 0$, m_ℓ can only be 0. For $\ell = 1$, the absolute value of m_ℓ must be less than or equal to 1, so for integers the only possibilities are 0, 1, and -1 (otherwise listed as -1, 0, 1). For $\ell = 2$, the possible integer values of m_ℓ are -2, -1, 0, 1, and 2. For $\ell = 3$, the possible m_ℓ values are -3, -2, -1, 0, 1, 2, and 3. For $\ell = 4$, the possible values of m_ℓ are -4, -3, -2, -1, 0, 1, 2, 3, and 4.

Because the quantum number m_ℓ can have integer values from $-\ell$ to ℓ including 0, there are $2\ell + 1$ possible values of m_ℓ for each value of ℓ.

Table 11.3 lists several of the associated Legendre polynomials. They are represented here as θ_{ℓ,m_ℓ}. It doesn't matter whether m_ℓ is positive or negative; its magnitude determines which polynomial is needed.

Now the two parts of the solution for equation 11.46 can be combined to get the entire solution for 3-D rotational motion. The acceptable wavefunctions are

$$\Psi = \frac{1}{\sqrt{2\pi}} e^{im_\ell \phi} \cdot \Theta_{\ell,m_\ell} \tag{11.49}$$

where the following conditions apply:

$$\ell = 0, 1, 2, 3, \ldots$$

$$|m_\ell| \leq \ell$$

These wavefunctions are functions that were well known to the people who developed quantum mechanics. They are called *spherical harmonics* and are labeled $Y^{\ell}_{m\ell}$ (or Y_{ℓ,m_ℓ}). Once again, classical mathematics anticipated quantum mechanics in the solution of differential equations. Although the Legendre polynomials do not distinguish between positive and negative values of the quantum number m, the exponential part of the complete wavefunction does. Each set of quantum numbers (ℓ, m_ℓ) therefore indicates a unique wavefunction, denoted Ψ_{ℓ,m_ℓ}, that can describe the possible state of a particle confined to the surface of a sphere. The wavefunction itself does *not* depend on either the mass of the particle or the radius of the sphere that defines the system.

Example 11.16

Show that the wavefunction $\Psi_{1,1}$ is normalized over all space. Use the associated Legendre polynomial listed in Table 11.3.

Solution

The complete wavefunction consists of the appropriate associated Legendre polynomial as well as the appropriate $(1/\sqrt{2\pi})e^{im_\ell \phi}$ part. The complete $\Psi_{1,1}$ wavefunction is

$$\Psi_{1,1} = \frac{1}{\sqrt{2\pi}} \cdot e^{i \cdot 1 \cdot \phi} \cdot \frac{1}{2}\sqrt{3} \sin \theta$$

which simplifies to

$$\Psi_{1,1} = \frac{\sqrt{3}}{2\sqrt{2\pi}} \cdot e^{i\phi} \sin \theta$$

The normalization requirement is that the integral of the square of the wavefunction over all space equals 1. So, we set up the wavefunction and integrate it over ϕ and θ:

$$\Psi_{1,1} = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \left(\frac{\sqrt{3}}{2\sqrt{2\pi}} \cdot e^{i\phi} \sin \theta \right)^{*} \frac{\sqrt{3}}{2\sqrt{2\pi}} \cdot e^{i\phi} \sin \theta \, d\phi \sin \theta \, d\theta$$

where the final sin θ term comes from the definition of $d\tau$ in this two-dimensional system.

$$\Psi_{1,1} = \frac{3}{4 \cdot 2\pi} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} e^{-i\phi} \sin \theta \, e^{i\phi} \sin \theta \, d\phi \sin \theta \, d\theta$$

The two exponentials cancel each other. Separating the remaining ϕ and θ parts into their respective integrals:

$$\Psi_{1,1} = \frac{3}{8\pi} \int_{\phi=0}^{2\pi} d\phi \int_{\theta=0}^{\pi} \sin^3 \theta \, d\theta$$

Each integral can be solved separately. The first integral, over ϕ, is easily shown to be

$$\int_{\phi=0}^{2\pi} d\phi = \phi\big|_0^{2\pi} = 2\pi - 0 = 2\pi$$

The second integral, over θ, must be either integrated by parts or looked up in an integrals table. This integral is included in Appendix 1.

$$\int_{\theta=0}^{\pi} \sin^3\theta\, d\theta = -\tfrac{1}{3}\cos\theta(\sin^2\theta + 2)\big|_0^{\pi}$$
$$= -\tfrac{1}{3}[(-1)(0+2) - (1)(0+2)] = \tfrac{4}{3}$$

If we combine all terms from the integral, we find

$$\Psi_{1,1} = \frac{3}{8\pi} \cdot 2\pi \cdot \frac{4}{3} = 1$$

confirming that the spherical harmonic wavefunction is indeed normalized.

Using the explicit forms of the spherical harmonics, one can use standard trigonometric integrals to show that the wavefunctions are also orthogonal to each other. That is,

$$\int \Psi^*_{\ell,m_\ell}\Psi_{\ell',m'_\ell}\, d\tau = 0 \quad \text{unless} \quad \ell = \ell' \quad \text{and} \quad m_\ell = m_{\ell'} \qquad \textbf{(11.50)}$$

The energy eigenvalues for 3-D rotational motion can be determined analytically by putting the spherical harmonics into the Schrödinger equation and solving for the energy. It is a straightforward mathematical procedure (see exercise 11.33), but here we are more interested in the analytic expression for the energy. It is

$$E \equiv E(\ell) = \frac{\ell(\ell+1)\hbar^2}{2I} \qquad \textbf{(11.51)}$$

The energy of 3-D rotational motion depends on the particle's moment of inertia, Planck's constant, and ℓ. Since the total energy cannot have any values other than these, *the total energy is quantized* and depends on the quantum number ℓ. It does *not* depend on m_ℓ. Therefore, each energy level is $(2\ell + 1)$-fold degenerate.

The expression for the energy of a 3-D rotation is slightly different from the energy levels of a 2-D rotation. Because of the $\ell + 1$ term in the numerator, the energy of a 3-D rotation goes up slightly faster with the quantum number ℓ than does the energy of a 2-D rotation versus m. This is illustrated by Figure 11.13, which diagrams the first eight energy levels of both the 2-D and 3-D rotations.

A *3-D rigid rotor* is a system of more than one particle having fixed relative positions (that is, a molecule) that is rotating in three-dimensional space. The only change in any of the expressions derived above is the substitution of μ, the reduced mass, for m, the mass. (Be careful to not confuse mass and rotational quantum number, both of which can be represented by m.) The wavefunctions, energy eigenvalues, and angular momentum eigenvalues can be determined using the same expressions after substitution for μ.

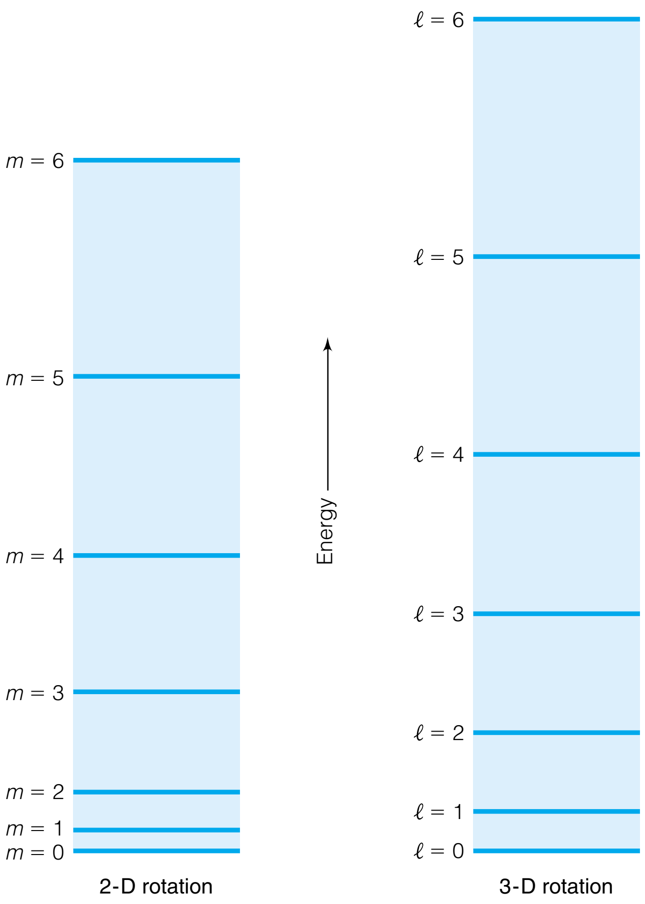


Figure 11.13 A comparison of the 2-D and 3-D rotations' quantized energies. The drawing is to scale vertically. 3-D rotations have slightly more energy than 2-D rotations of the same quantum number.

Example 11.17

The carbon molecule buckminsterfullerene, C_{60}, can be approximated as a sphere, and the electrons of the molecule can be thought of as being confined to the surface of a sphere. If one of the absorptions of C_{60} corresponds to an electron going from the $\ell = 4$ state to the $\ell = 5$ state, what wavelength of light would cause this change? Use $r = 3.50$ Å to calculate the moment of inertia. (A transition in the C_{60} spectrum is seen at 404 nm).

Solution

The moment of inertia of an electron in this system is

$$I = (9.109 \times 10^{-31}\ \text{kg})(3.50 \times 10^{-10}\ \text{m})^2 = 1.12 \times 10^{-49}\ \text{kg}\cdot\text{m}^2$$

The energy of the $\ell = 4$ state is therefore

$$E(\ell = 4) = \frac{4(4 + 1)(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})^2}{2 \cdot 1.12 \times 10^{-49}\ \text{kg}\cdot\text{m}^2 \cdot (2\pi)^2} = 9.93 \times 10^{-19}\ \text{J}$$

and the energy for the $\ell = 5$ state is

$$E(\ell = 5) = \frac{5(5 + 1)(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})^2}{2 \cdot 1.12 \times 10^{-49}\ \text{kg}\cdot\text{m}^2 \cdot (2\pi)^2} = 1.49 \times 10^{-18}\ \text{J}$$

The difference in the energies is

$$\Delta E = 4.96 \times 10^{-19}\ \mathrm{J}$$

Using $E = h\nu$, it can be shown that this energy difference corresponds to the absorption of a photon having frequency ν of

$$\nu = 7.49 \times 10^{14}\ \mathrm{s}^{-1}$$

Using $c = \lambda\nu$, this frequency corresponds to a wavelength of

$$\lambda = 4.00 \times 10^{-7}\ \mathrm{m}$$

which is 400. nm. This compares very well to the experimentally measured absorption appearing at 404 nm.

The above example shows that the 3-D rotational model is applicable to a real system, just as the particle-in-a-box and 2-D rotational motion can be applied to real systems. Other transitions of C_{60} can also be fit to the 3-D rotation equations, but they are left for exercises. These examples show that even though these are model systems, they do have application to the real world. The situation is similar to that of the ideal gas: we have equations to express the behavior of an ideal gas. And although there is no such thing as an ideal gas, real gases can approximate ideal gas behavior, so ideal gas equations have a useful purpose in real life. These equations from quantum mechanics have the same applicability as the equations for an ideal gas. These model systems do not exist in reality, but some atomic or molecular systems do exist that can be approximated with these systems. The quantum mechanical equations work reasonably well. They work much better than anything that classical mechanics could ever have provided.

11.8 Other Observables in Rotating Systems

There are other observables to consider, starting with the total angular momentum. The operator is $\hat{L}^2$, so the eigenvalue will be the square of the total angular momentum. Since the total energy can be written in terms of the square of the total angular momentum, it should be no surprise that the spherical harmonics are also eigenfunctions of (total angular momentum)^2. Like the energy eigenvalues, the analytic demonstration of the eigenvalue equation is complex. Here, only the ultimate result is presented:

$$\hat{L}^2\Psi_{\ell,m_\ell} = \ell(\ell + 1)\hbar^2\Psi_{\ell,m_\ell} \tag{11.52}$$

The square of the total angular momentum has the value $\ell(\ell + 1)\hbar^2$. The total angular momentum is the square root of this expression, so the total, three-dimensional angular momentum of any state described by the quantum numbers ℓ and m_ℓ is

$$L = \sqrt{\ell(\ell + 1)}\hbar \tag{11.53}$$

The total angular momentum is not dependent on the m_ℓ quantum number. Nor is it dependent on the mass of the particle, or the dimension of the sphere. These ideas are again counter to the concepts of classical mechanics.

Example 11.18

What are the total angular momenta of an electron in the $\ell = 4$ and $\ell = 5$ states of C_{60} (see Example 11.17 above)?

Solution

According to equation 11.53, the total angular momentum is dependent only on ℓ and $\hbar$. For $\ell = 4$ and 5, the angular momenta of the electrons are

$$L(\ell = 4) = \sqrt{4(4+1)}(6.626 \times 10^{-34}\ \text{J·s})/2\pi$$

$$L(\ell = 5) = \sqrt{5(5+1)}(6.626 \times 10^{-34}\ \text{J·s})/2\pi$$

Evaluating the above expressions:

$$L(\ell = 4) = 4.716 \times 10^{-34}\ \text{J·s}$$

$$L(\ell = 5) = 5.776 \times 10^{-34}\ \text{J·s}$$

There is a third observable of interest. It is the z component of the total angular momentum, L_z. The relationships between angular momentum operators allow for the simultaneous knowledge of the total angular momentum (through its square, L^2) and *one* of its Cartesian components. By convention, the z component is chosen. This is due in part to the spherical polar coordinate system, and the relatively simple definition of the z component of the angular momentum in terms of ϕ, as seen in the discussion of the 2-D rotating system.

As before, the z component of angular momentum is defined as

$$\widehat{L}_z = -i\hbar\frac{\partial}{\partial\phi} \tag{11.54}$$

This is the same operator we used for 2-D rotation. Since the ϕ part of the 3-D rotational wavefunction is exactly the same as for the 2-D rotational wavefunction, it may not surprise you that the eigenvalue equation, and therefore the value of the observable L_z, is exactly the same:

$$\widehat{L}_z\Psi = m_\ell\hbar\Psi \tag{11.55}$$

The z component of the three-dimensional angular momentum, which has components in the x, y, and z direction, is *quantized.* Its quantized value depends on the m_ℓ quantum number.

L_z is only one component of the total angular momentum L. The other components are L_x and L_y. However, the principles of quantum mechanics do not allow us to know quantized values for these two components simultaneously with L_z. Therefore, only one of the three components of the total angular momentum can have a known eigenvalue simultaneously with the L^2 itself. For convenience, we choose the z component of the angular momentum, L_z, to be the knowable observable.*

Graphically, the quantized total and z-component angular momenta are illustrated in Figure 11.14. The length of each vector represents the total angular momentum and is the same for all five vectors where $\ell = 2$. However, the z components of the five vectors are different, each one indicating a different value of the m_ℓ quantum number (from -2 to 2). This figure also illustrates that all of the momentum cannot be completely in the z direction, since there is no nonzero integer W such that $W = \sqrt{(W)(W+1)}$.

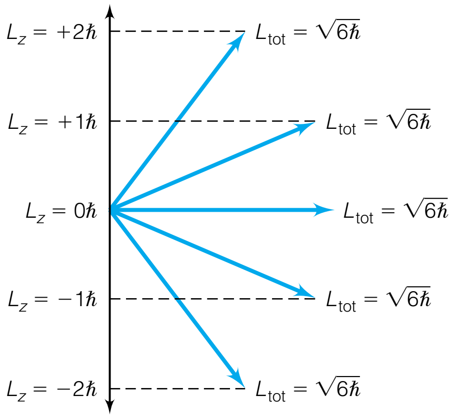


Figure 11.14 The same quantized value for L can have different quantized values for L_z. For $\ell = 2$, there are $2\ell + 1 = 5$ possible values of m_ℓ, each having a different value of L_z.

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*Technically, we could choose the x or y component of the total angular momentum to be the knowable observable, but the z component is typically chosen if one dimension is unique compared to the other two.

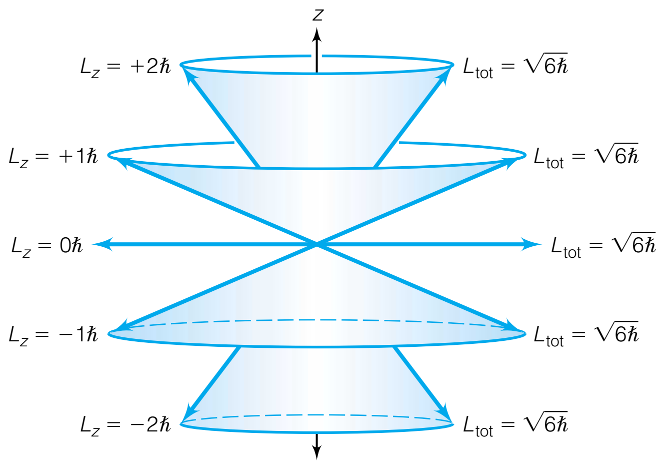


Figure 11.15 Because quantum mechanics does not address the angular momentum components in the x or y dimension, the proper diagram relating L and L_z is a cone, where the total angular momentum and the z component of the total angular momentum are quantized, but the x and y components are indeterminate and can have any value.

Since the values of L_x and L_y are indeterminate for specified ℓ and m_ℓ, the graphical representations of Figure 11.14 are better represented three-dimensionally as cones instead of vectors. Such a representation is shown in Figure 11.15. This figure shows the angular momentum vectors superimposed on a sphere, representing our 3-D surface. Again, the "length" of each cone is constant. The orientation of each cone with respect to the z-axis is different, and is determined by the value of the m_ℓ quantum number.

Since the energy of 3-D rotational motion depends only on the quantum number ℓ and ℓ has $2\ell + 1$ possible values of m_ℓ, each energy level has a degeneracy of $2\ell + 1$.

Example 11.19

What are the degeneracies of the $\ell = 4$ and $\ell = 5$ levels for C_{60} if the electrons are assumed to behave like particles confined to the surface of a sphere?

Solution

The $\ell = 4$ energy level has $2(4) + 1 = 9$ possible values of m_ℓ, so this energy level has a degeneracy of 9. Similarly, the $\ell = 5$ energy level has a degeneracy of 11.

Example 11.20

Construct the complete spherical harmonic for $\Psi_{3,+3}$ and use the operators for E, L^2, and L_z to explicitly determine the energy, the total angular momentum, and the z-component angular momentum. Show that the values of these observables are equal to those predicted by the analytic expressions for E, L^2, and L_z. (The objective of this example is to illustrate that the operators do in fact operate on the wavefunction to produce the appropriate eigenvalue equation.)

Solution

The complete spherical harmonic $\Psi_{3,+3}$ is given by

$$\Psi_{3,+3} = \frac{\sqrt{70}}{8\sqrt{2\pi}} e^{+3i\phi} \sin^3 \theta$$

Let us consider the total angular momentum first, since we can use the results of those manipulations to get the total energy. The total angular momentum can be determined from

$$\hat{L}^2\Psi = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\Psi$$

Taking derivatives first with respect to θ, one finds

$$\frac{\partial}{\partial\theta}\left(\frac{\sqrt{70}}{8\sqrt{2\pi}} e^{+3i\phi} \sin^3\theta\right) = \frac{3\sqrt{70}}{8\sqrt{2\pi}} e^{+3i\phi} \sin^2\theta\cos\theta$$

$$\frac{\partial^2}{\partial\theta^2}\left(\frac{\sqrt{70}}{8\sqrt{2\pi}} e^{+3i\phi} \sin^3\theta\right) = \frac{3\sqrt{70}}{8\sqrt{2\pi}} e^{+3i\phi} (2\cos^2\theta\sin\theta - \sin^3\theta)$$

The derivative with respect to ϕ is simply

$$\frac{\partial^2}{\partial\phi^2}\left(\frac{\sqrt{70}}{8\sqrt{2\pi}} e^{+3i\phi} \sin^3\theta\right) = 3^2 i^2\frac{\sqrt{70}}{8\sqrt{2\pi}} e^{+3i\phi} \sin^3\theta$$

$$= -9\frac{\sqrt{70}}{8\sqrt{2\pi}}e^{+3i\phi} \sin^3\theta$$

Putting all this together, one gets

$$\hat{L}^2\Psi = -\hbar^2\left[\frac{3\sqrt{70}}{8\sqrt{2\pi}} e^{+3i\phi}(2\cos^2\theta\sin\theta - \sin^3\theta) + \cot\theta\frac{3\sqrt{70}}{8\sqrt{2\pi}} e^{+3i\phi}\sin^2\theta\cos\theta + \frac{1}{\sin^2\theta}\left(-9\frac{\sqrt{70}}{8\sqrt{2\pi}}e^{+3i\phi}\right)\right]$$

This can be simplified by factoring out the wavefunction constants and the exponential from all of the terms to get

$$\hat{L}^2\Psi = -\hbar^2\left[3(2\cos^2\theta\sin\theta - \sin^3\theta) + 3\cot\theta\sin^2\theta\cos\theta - 9\frac{1}{\sin^2\theta}\sin^3\theta\right]\frac{\sqrt{70}}{8\sqrt{2\pi}}e^{+3i\phi}$$

Simplifying all the terms and remembering the definition of the cotangent:

$$\hat{L}^2\Psi = -\hbar^2(6\cos^2\theta\sin\theta - 3\sin^3\theta + 3\sin\theta\cos^2\theta - 9\sin\theta)\frac{\sqrt{70}}{8\sqrt{2\pi}}e^{+3i\phi}$$

$$= -\hbar^2(9\cos^2\theta\sin\theta - 3\sin^3\theta - 9\sin\theta)\frac{\sqrt{70}}{8\sqrt{2\pi}}e^{+3i\phi}$$

Substituting for the trigonometric identity $\cos^2\theta = 1 - \sin^2\theta$:

$$\hat{L}^2\Psi = -\hbar^2[9(1 - \sin^2\theta)\sin\theta - 3\sin^3\theta - 9\sin\theta]\frac{\sqrt{70}}{8\sqrt{2\pi}}e^{+3i\phi}$$

$$= -\hbar^2(9\sin\theta - 9\sin^3\theta - 3\sin^3\theta - 9\sin\theta)\frac{\sqrt{70}}{8\sqrt{2\pi}}e^{+3i\phi}$$

$$= -\hbar^2(-12 \sin^3 \theta) \frac{\sqrt{70}}{8\sqrt{2\pi}} e^{+3i\phi}$$

$$= 12\hbar^2\Psi_{3,+3}$$

So, invoking the postulate that the value of an observable is equal to the eigenvalue from the corresponding eigenvalue equation:

$$\hat{L}^2\Psi_{3,+3} = 12\hbar^2\Psi_{3,+3}$$

or

$$L^2 = 12\hbar^2$$

Since the eigenvalue of the square of the total angular momentum is $12\hbar^2$, the value of the total angular momentum must be the square root of this, or $\sqrt{12}\hbar$. This value, numerically, is 3.653×10^{-34} J·s, or 3.653×10^{-34} kg·m^2/s. The value for the energy can be determined from

$$E = \frac{L^2}{2I}$$

which is

$$E = \frac{12\hbar^2}{2I}$$

The exact numerical value of the total energy will depend on the moment of inertia of the system (which is not given, so we cannot calculate the energy numerically). The z component of the angular momentum, L_z, is determined by the eigenvalue equation

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}\Psi_{3,+3} = -i\hbar\frac{\partial}{\partial\phi}\left(\frac{\sqrt{70}}{8\sqrt{2\pi}}e^{+3i\phi} \sin^3 \theta\right)$$

$$= -i\hbar(3i)\left(\frac{\sqrt{70}}{8\sqrt{2\pi}} e^{+3i\phi} \sin^3 \theta\right) = 3\hbar\left(\frac{\sqrt{70}}{8\sqrt{2\pi}}e^{+3i\phi} \sin^3 \theta\right)$$

$$= 3\hbar\Psi_{3,+3}$$

So the value of the z component of the angular momentum is given by the eigenvalue $3\hbar$, which equals 3.164×10^{-34} J·s.

In all three cases, the predicted observables are the same as those determined by the analytic formulas of each observable.

It would have been easier (and shorter!) to use the formulas for the energy and momenta to determine the values of these three quantized observables. But it is important to understand that these differential equations actually do work when the wavefunctions are operated on by them. The above example shows that all of the operators do yield the appropriate values of the observables.

There are a few other analytically solvable systems, but most are variations on the themes presented here and in the last chapter. For now, we will halt our treatment of model systems and move on to a system that is more obviously relevant chemically. But before we do, it is important to re-emphasize a few conclusions about the systems we have treated so far. (1) In all of our model systems, the total energy (kinetic + potential) is quantized. This is a result of the postulates of quantum mechanics. (2) In some of the systems, other observables are also quantized and have analytic expressions for their quantized values (like momentum). Whether other observables have analytic expressions for their quantized values depends on the system. *Average values,* rather than quantized values, may be all that can be determined. (3) All of these model systems have approximate analogs in reality, so that the conclusions obtained from the analysis of these systems can be applied approximately to known chemical systems (much in the same way ideal gas laws are applied to the behavior of real gases). (4) Classical mechanics was unable to rationalize these observations of atomic and molecular systems. It is this last point that makes quantum mechanics worth understanding in order to understand chemistry.

11.9 The Hydrogen Atom: A Central Force Problem

It is a very short jump from the 3-D rigid rotor to the hydrogen atom. Hydrogen is nothing more than a nucleus (a single proton) and an electron "in orbit" about the nucleus. For a two-particle system with the motion occurring relatively (that is, the electron is usually considered as moving around the nucleus), the reduced mass must be used in any expression where mass would appear. Instead of simple electronic motion, it is more properly thought of as motion of two particles about a common center of mass. (The reduced mass is very similar to the mass of the electron, but the difference is measurable.)

The final part of the quantum-mechanical description of the hydrogen atom system deals with the third spherical polar coordinate r. In the 3-D rigid rotor, we assumed a constant r. In earlier treatments of atoms (specifically, the Bohr theory of the hydrogen atom), electrons were naively assumed to have fixed orbits about nuclei. Classical mechanics provided the background for such an assumption. Consider a rock tied to the end of a rope, swirled above your head. Since you grip the rope tightly, of course the rock spins at a constant radius! It would be contrary to experience to think that the radius of the rope changes as the weight spins. Other circular motion reinforces this reasoning: merry-go-rounds, Ferris wheels, automobile tires, spinning tops—almost every circular motion in our experience occurs at some fixed distance from an axis.

Consider the atomic scale, however. The uncertainty principle suggests that specifying a certain position of an electron is incompatible with other observables that we use to describe the state of the electron, like momentum and energy. Maybe we *can't* fix the electron to a certain radius.

A proper quantum-mechanical treatment of H makes no presumptions about the distance of an electron from a nucleus. Thus, the description of the hydrogen atom is the same as for the 3-D rigid rotor except it includes variation of r, which ranges from 0 to ∞. This is illustrated in Figure 11.16. The hydrogen atom is defined like a 3-D rigid rotor, only now the radius can vary also. Wavefunctions describing the motion of an electron in a hydrogen atom must therefore satisfy the 3-D spherical polar Schrödinger equation

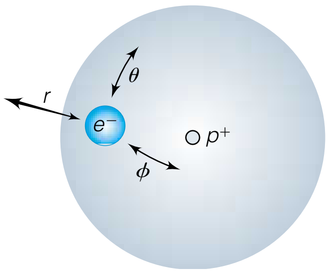


Figure 11.16 The hydrogen atom, as defined in quantum mechanics. This system is defined similarly to the 3-D rigid rotor (Figure 11.11) except now r can vary.

$$\left\{-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]+\hat{V}\right\}\Psi = E\Psi \qquad (11.56)$$

where the form of the Hamiltonian operator reflects the fact that all three spherical polar coordinates, r, θ, and ϕ, can vary. Note the relationship between equations 11.56 and 11.46, where the spherical polar coordinate r is not changing. Also note that we are using the reduced mass μ in the Schrödinger equation, not the mass of the electron.

In the case of the hydrogen atom, the potential energy is not zero. There is an interaction between the electron and the nucleus for this system. The interaction is electrostatic; that is, it is due to the attraction between the positively charged nucleus and the negatively charged electron. Fortunately, such an electrostatic potential energy has a known mathematical formula, based ultimately on the ideas of Coulomb:

$$V = \frac{-e^2}{4\pi\epsilon_0 r} \tag{11.57}$$

where $e = 1.602 \times 10^{-19}$ coulombs, ϵ_0 is the permittivity of free space and equals 8.854×10^{-12} $\mathrm{C^2/J \cdot m}$, and r is the distance between the two charged particles. From this, it is easy to show that the expression for V in equation 11.57 yields units of J, a unit of energy.

The potential energy V depends only on the distance r separating the nucleus and the electron, not the angles θ or ϕ. This means that the potential energy is the same at a fixed r no matter what the values of θ or ϕ are. That is to say, the potential energy is *spherically symmetric.* The force between the electron and the hydrogen nucleus is also spherically symmetric. Because of this, the force is said to be a *central force,* and the hydrogen atom description in quantum mechanics is an example of what is generally known as a *central force problem.*

The complete Schrödinger equation for this central force problem is thus

$$\left\{-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] + \frac{-e^2}{4\pi\epsilon_0 r}\right\}\Psi = E\Psi \tag{11.58}$$

and acceptable wavefunctions for a hydrogen atom must satisfy this Schrödinger equation. It should be noted that there is another way to write this Schrödinger equation, using the total angular momentum operator $\hat{L}^2$:

$$\left\{-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right] + \frac{1}{2\mu r^2}\hat{L}^2 + \frac{-e^2}{4\pi\epsilon_0 r}\right\}\Psi = E\Psi \tag{11.59}$$

11.10 The Hydrogen Atom: The Quantum-Mechanical Solution

A detailed mathematical solution of equations 11.58 or 11.59 is not presented here, but the approach will be explained. As with the 3-D rotational motion, it will be assumed that acceptable wavefunctions Ψ are separable into three functions that depend only on r, on θ, and on ϕ:

$$\Psi(r, \theta, \phi) = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi)$$

It may not be surprising to learn that the Θ and Φ parts of the wavefunction Ψ are the spherical harmonics, discussed earlier for the 3-D rigid rotor. These solutions impose two integers called quantum numbers, ℓ and m_ℓ, which determine the exact mathematical expression. Because the Schrödinger equation can be written in terms of the total angular momentum operator $\hat{L}^2$, we can substitute the solutions for that part of the operator into the Schrödinger equation and get a differential equation in terms of r and R alone:

$$\left\{\frac{-\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right] + \frac{\hbar^2\ell(\ell + 1)}{2\mu r^2} + \frac{-e^2}{4\pi\epsilon_0 r}\right\}R = ER \tag{11.60}$$

The influence of the spherical harmonics part of the complete wavefunction is seen in the second term on the left. Although this is a differential equation in terms of r only, the quantum number ℓ is present. This suggests that the solution to this differential equation depends on the quantum number ℓ just like the quantum number m_ℓ depends on ℓ in the spherical harmonics.

The solutions to the differential equation 11.60 were known, just as the spherical harmonics were known. One part of the solution of R is an exponential function with a negative exponent, similar to the solution for the harmonic oscillator. The exponential that works in this case is $e^{-r/na}$, where n is a positive integer and a is the collection of constants given by

$$a = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$

where all the constants in the definition of a have their usual meanings. We will see more of this expression later. These exponentials are multiplying a polynomial, again in a situation similar to the harmonic oscillator wavefunctions, which composes the rest of the solution to the differential equation 11.60. The polynomial is one of a set of polynomials that have varying numbers of terms and are called the *associated Laguerre polynomials.* A positive integer index labels each associated Laguerre polynomial, and it is usually indicated by the letter n. This n has the same value as the n in the exponential part of the solution for R. Also, for each n there may be several Laguerre polynomials, each one having a different value of ℓ (the quantum number from 3-D rotational motion). But not just any value of ℓ: the associated Laguerre polynomials restrict the possible values of ℓ to any integer such that

$$\ell < n$$

Therefore, the integer n restricts the possible integer values of ℓ (with 0 being the minimum value of ℓ). Since n is a positive integer, there is a simple series of ℓ values for each n:

n	possible ℓ's
1	0
2	0,1
3	0,1,2
4	0,1,2,3
5	0,1,2,3,4
⋮	⋮

Since the possible values of m_ℓ are restricted by the specific value of ℓ, n ultimately restricts the values of m_ℓ also. However, we again see that the restriction arises due to the inherent restrictions on the allowed mathematical solutions of the Schrödinger equation.

The complete wavefunction for the hydrogen atom is a combination of the spherical harmonic, $Y^{\ell}_{m_\ell} = (1/\sqrt{2\pi})e^{im_\ell\phi} \cdot \Theta_{\ell,m_\ell}$, and the exponential-associated Laguerre polynomial combination, which is denoted $R_{n,\ell}$:

$$\Psi(r, \theta, \phi) = R_{n,\ell} \cdot Y^{\ell}_{m_\ell} = \frac{1}{\sqrt{2\pi}}e^{im_\ell\phi} \cdot \Theta_{\ell,m_\ell} \cdot R_{n,\ell} \tag{11.61}$$

with the following restrictions:

$$\begin{aligned} n &= 1, 2, 3, \ldots \\ \ell &< n \\ |m_\ell| &\le \ell \end{aligned} \tag{11.62}$$

Table 11.4 Complete wavefunctions for hydrogen-like atoms[a]

n	ℓ	m_ℓ	Ψ_{n,ℓ,m_ℓ}
1	0	0	$\left(\frac{Z^3}{\pi a^3}\right)^{1/2} e^{-Zr/a}$
2	0	0	$\frac{1}{8}\left(\frac{2Z^3}{\pi a^3}\right)^{1/2}\left(2-\frac{Zr}{a}\right)e^{-Zr/2a}$
2	1	-1	$\frac{1}{8}\left(\frac{2Z^3}{\pi a^3}\right)^{1/2}\frac{Zr}{a}e^{-Zr/2a}\sin\theta\cdot e^{-i\phi}$
2	1	0	$\frac{1}{8}\left(\frac{2Z^3}{\pi a^3}\right)^{1/2}\frac{Zr}{a}e^{-Zr/2a}\cos\theta$
2	1	$+1$	$\frac{1}{8}\left(\frac{2Z^3}{\pi a^3}\right)^{1/2}\frac{Zr}{a}e^{-Zr/2a}\sin\theta\cdot e^{i\phi}$
3	0	0	$\frac{1}{243}\left(\frac{3Z^3}{\pi a^3}\right)^{1/2}\left(27-\frac{18Zr}{a}+\frac{2Zr^2}{a^2}\right)e^{-Zr/3a}$
3	1	-1	$\frac{1}{81}\left(\frac{Z^3}{\pi a^3}\right)^{1/2}\frac{Zr}{a}\left(6-\frac{Zr}{a}\right)e^{-Zr/3a}\sin\theta\cdot e^{-i\phi}$
3	1	0	$\frac{1}{81}\left(\frac{2Z^3}{\pi a^3}\right)^{1/2}\frac{Zr}{a}\left(6-\frac{Zr}{a}\right)e^{-Zr/3a}\cos\theta$
3	1	1	$\frac{1}{81}\left(\frac{Z^3}{\pi a^3}\right)^{1/2}\frac{Zr}{a}\left(6-\frac{Zr}{a}\right)e^{-Zr/3a}\sin\theta\cdot e^{i\phi}$
3	2	-2	$\frac{1}{162}\left(\frac{Z^3}{\pi a^3}\right)^{1/2}\frac{Z^2r^2}{a^2}e^{-Zr/3a}\sin^2\theta\cdot e^{-2i\phi}$
3	2	-1	$\frac{1}{81}\left(\frac{Z^3}{\pi a^3}\right)^{1/2}\frac{Z^2r^2}{a^2}e^{-Zr/3a}\sin\theta\cos\theta\cdot e^{-i\phi}$
3	2	0	$\frac{1}{486}\left(\frac{6Z^3}{\pi a^3}\right)^{1/2}\frac{Z^2r^2}{a^2}e^{-Zr/3a}(3\cos^2\theta-1)$
3	2	$+1$	$\frac{1}{81}\left(\frac{Z^3}{\pi a^3}\right)^{1/2}\frac{Z^2r^2}{a^2}e^{-Zr/3a}\sin\theta\cos\theta\cdot e^{i\phi}$
3	2	$+2$	$\frac{1}{162}\left(\frac{Z^3}{\pi a^3}\right)^{1/2}\frac{Z^2r^2}{a^2}e^{-Zr/3a}\sin^2\theta\cdot e^{2i\phi}$

[a] $a = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$

For convenience, several of the first few wavefunctions are listed in Table 11.4 along with their respective n, ℓ, and m_ℓ quantum numbers. Each characteristic set (n, ℓ, m_ℓ) refers to a specific wavefunction. It is easy to show that for any n, the total number of possible wavefunctions having that value of n is n^2. (This will increase by a factor of 2 when we include the spin of the electron, but that will be considered in Chapter 12.)

The eigenvalue for energy also has an analytic solution. It is

$$E = -\frac{e^4\mu}{8\epsilon_0^2h^2n^2} \tag{11.63}$$

The energy is *negative* here. This is due to the convention that the interaction of oppositely charged particles contributes to a decrease in energy. (Conversely, the repulsion of similarly charged particles would be positive in energy.) An energy of zero corresponds to the proton and electron at infinite distance from each other (so that the potential energy is zero) and having no kinetic energy with respect to each other. The energy depends on a collection of constants—the charge on the electron, e , the reduced mass of the hydrogen atom μ, the permittivity of free space ϵ_0, Planck's constant h—and the integer n. The energy depends on the index n; n is a quantum number and the total energy is quantized. The energy of the hydrogen atom does not depend on the quantum numbers ℓ or m_ℓ, only on n. The index n is therefore called the *principal* *quantum number.* Because n^2 wavefunctions have the same quantum number n, the degeneracy of each energy state of the hydrogen atom is n^2. (Again, this will change by a factor of 2.) Each set of wavefunctions having the same value for the principal quantum number is said to define a *shell.*

Example 11.21

Calculate the energy values for the first three shells of the hydrogen atom. The reduced mass of the hydrogen atom is 9.104×10^{-31} kg.

Solution

Values are substituted into equation 11.63 for $n = 1$, 2, and 3:

$$E = -\frac{(1.602 \times 10^{-19}\ \mathrm{C})^4(9.104 \times 10^{-31}\ \mathrm{kg})}{8[8.854 \times 10^{-12}\ \mathrm{C^2/(J\cdot m)}]^2(6.626 \times 10^{-34}\ \mathrm{J\cdot s})^2 1^2}$$

$$E = -\frac{(1.602 \times 10^{-19}\ \mathrm{C})^4(9.104 \times 10^{-31}\ \mathrm{kg})}{8[8.854 \times 10^{-12}\ \mathrm{C^2/(J\cdot m)}]^2(6.626 \times 10^{-34}\ \mathrm{J\cdot s})^2 2^2}$$

$$E = -\frac{(1.602 \times 10^{-19}\ \mathrm{C})^4(9.104 \times 10^{-31}\ \mathrm{kg})}{8[8.854 \times 10^{-12}\ \mathrm{C^2/(J\cdot m)}]^2(6.626 \times 10^{-34}\ \mathrm{J\cdot s})^2 3^2}$$

These expressions give

$$E(n = 1) = 2.178 \times 10^{-18}\ \mathrm{J}$$

$$E(n = 2) = 5.445 \times 10^{-19}\ \mathrm{J}$$

$$E(n = 3) = 2.420 \times 10^{-19}\ \mathrm{J}$$

where it can easily be shown that the units are joules:

$$\frac{\mathrm{C^4\cdot kg}}{[\mathrm{C^2/(J\cdot m)}]^2(\mathrm{J\cdot s})^2} = \frac{\mathrm{C^4\cdot kg\cdot J^2\cdot m^2}}{\mathrm{C^4\cdot J^2\cdot s^2}} = \frac{\mathrm{kg\cdot m^2}}{\mathrm{s^2}} = \mathrm{J}$$

Remember that spectroscopy measures the changes in energy between two states. Quantum mechanics can also be used to determine a change in energy, ΔE, for the hydrogen atom:

$$E(n_1) - E(n_2) \equiv \Delta E = -\frac{e^4\mu}{8\epsilon_0^2 h^2 n_1^2} - \left(-\frac{e^4\mu}{8\epsilon_0^2 h^2 n_2^2}\right)$$

where the principal quantum numbers n_1 and n_2 are used to differentiate between the two energy levels involved. A little algebraic rearranging yields

$$\Delta E = \frac{e^4\mu}{8\epsilon_0^2 \mathrm{h}^2}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{11.64}$$

This is the same form of equation that Balmer got by considering the spectrum of hydrogen, and that Bohr got by assuming quantized angular momentum! In fact, the collection of constants multiplying the quantum number expression is familiar:

$$\frac{e^4\mu}{8\epsilon_0^2 h^2} = \frac{(1.602 \times 10^{-19}\ \mathrm{C})^4(9.104 \times 10^{-31}\ \mathrm{kg})}{8[8.854 \times 10^{-12}\ \mathrm{C^2/(J\cdot m]^2}(6.626 \times 10^{-34}\ \mathrm{J\cdot s})^2}$$

$$= 2.178 \times 10^{-18}\ \mathrm{J}$$

which is easily shown to be, in units of wavenumbers and to four significant figures,

$$\frac{e^4\mu}{8\epsilon_0^2h^2} = 109{,}700 \text{ cm}^{-1}$$

This is the Rydberg constant, R_H, from the hydrogen atom spectrum.* *Quantum mechanics therefore predicts the experimentally determined hydrogen atom spectrum.* At this point, quantum mechanics predicts everything that Bohr's theory did and more, and so supersedes the Bohr theory of the hydrogen atom.

Since the spherical harmonics are part of the hydrogen atom's wavefunctions, it should come as no surprise that the total angular momentum and the z component of the total angular momentum are also observables that have known analytic and quantized values. They are

$$\hat{L}^2\Psi_{n,\ell,m_\ell} = \ell(\ell + 1)\hbar^2\Psi_{n,\ell,m_\ell}$$
$$\hat{L}_z\Psi_{n,\ell,m_\ell} = m_\ell\hbar\Psi_{n,\ell,m_\ell}$$

so that the quantized values for total angular momentum are $\sqrt{\ell(\ell + 1)}\hbar$ and for the z component are $m_\ell\hbar$. The quantum number ℓ is called the *angular momentum quantum number.* The m_ℓ quantum number is the *z-component angular momentum quantum number,* sometimes called the magnetic quantum number due to the differing behavior of wavefunctions having different m_ℓ values in a magnetic field (another topic for later). The angular momentum of the hydrogen atom (due mostly to the electron) is quantized, as Bohr assumed. However, the exact values of the quantized angular momentum are slightly different than what Bohr assumed. It was not possible to know this in 1913, however, and though ultimately incorrect, Bohr's theory should be remembered as a crucial step in the right direction.

This treatment of the hydrogen atom is also applicable to any atom that has only one electron. In cases of other atoms, the nuclear charge is different and the overall atom itself has a charge. The atomic number, Z, and the reduced mass μ are the only changes in any of the equations from above (and the reduced mass approaches the mass of the electron as the nucleus gets larger). The Schrödinger equation for these *hydrogen-like* ions is

$$\left\{\frac{-\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] + \frac{-Ze^2}{4\pi\epsilon_0 r}\right\}\Psi = E\Psi \tag{11.65}$$

where Z shows up only in the potential energy. The only other major change is in the expression for the quantized energy of these ions, which now has the form

$$E = -\frac{Z^2e^4\mu}{8\epsilon_0^2h^2n^2} \tag{11.66}$$

The wavefunctions themselves also have a Z dependence on them. Table 11.4 gives the complete wavefunctions with their Z dependence already included. (In our previous treatment of the hydrogen atom, Z was 1.) The angular momenta observables have the same forms as given above. Spectra of the hydrogen-like ions, which have been observed experimentally, are as simple as that

---

*Using modern values of the fundamental constants and to eight significant figures, $R_H = 109{,}677.58 \text{ cm}^{-1}$.

of the hydrogen atom. The transitions appear at different wavelengths of light, however.

Example 11.22

Predict the wavelength of light emitted by an excited Li^{2+} ion ($Z = 3$) as an electron goes from the $n = 4$ state to the $n = 2$ state. Use the mass of the electron in place of the reduced mass (this imparts a very minor 0.008% error in the calculation).

Solution

We can use an expression for ΔE similar to the one in equation 11.64, with addition of the Z^2 term:

$$\Delta E = \frac{Z^2 e^4 \mu}{8\epsilon_0^2 h^2}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

For $n_2 = 2$ and $n_1 = 4$:

$$\Delta E = \frac{3^2(1.602 \times 10^{-19}\ \text{C})^4(9.104 \times 10^{-31}\ \text{kg})}{8[8.854 \times 10^{-12}\ \text{C}^2/(\text{J}\cdot\text{m})]^2(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})^2}\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$\Delta E = 3.677 \times 10^{-18}\ \text{J}$$

Using $E = h\nu$ and $c = \lambda\nu$ as conversions, we can determine the wavelength of the photon having this energy:

$$\lambda = 54.0\ \text{nm}$$

This wavelength is in the vacuum ultraviolet region of the spectrum.

11.11 The Hydrogen Atom Wavefunctions

Let us take a closer look at the wavefunctions themselves to finish this chapter. Each wavefunction of a hydrogen atom is called an *orbital*. As mentioned, the energy of an electron in an orbital (that is, an electron having its motion described by a particular wavefunction) is dependent only on the principal quantum number n and a collection of physical constants. Each group of wavefunctions having the same value of the quantized energy defines a *shell*. Each shell has a degeneracy of n^2. Each group of same-ℓ wavefunctions (for every ℓ there are $2\ell + 1$ wavefunctions, having different values of m_ℓ) constitutes a *subshell*. In hydrogen and hydrogen-like atoms, all of the subshells within each shell have the same energy. This is illustrated in Figure 11.17. In labeling shells and subshells in hydrogen-like atoms (and other atoms, as we will see), we make use of the quantum numbers n and ℓ. The numerical value of the principal quantum number is used in the labeling, and for ℓ a letter designation is used:

ℓ	Letter designation
0	*s*
1	*p*
2	*d*
3	*f*
4	*g*
⋮	⋮

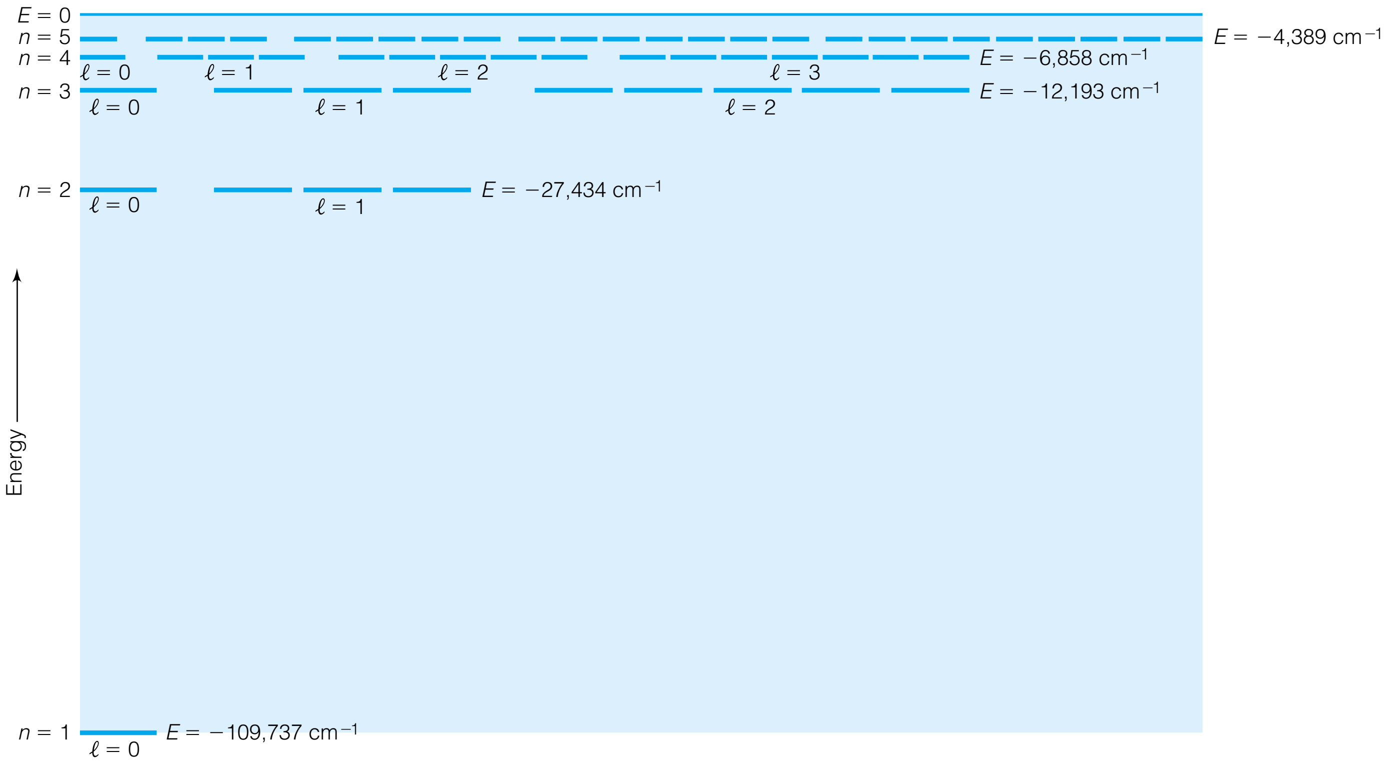


Figure 11.17 The energy level diagram for a hydrogen atom, showing the n and ℓ quantum numbers for the levels. The quantized energy levels are labeled. Degenerate wavefunctions are shown.

Orbitals are designated by pairing the value of the principal quantum number and the letter representing the value of ℓ: 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 3*d*, and so forth. A numerical subscript can be used to label the m_ℓ values of the individual orbitals: $2p_{-1}$, $2p_0$, $2p_{+1}$, and so on. Since the value of n restricts the value of ℓ, the first shell has only an *s* subshell (because ℓ can only be 0). The second shell has only *s* and *p* subshells (because ℓ can only be 0 or 1), and so forth. These restrictions are due to the nature of the mathematical solution of the Schrödinger equation.

Example 11.23

What are the possible subshells in the $n = 5$ shell? How many orbitals are in each subshell? Do not include m_ℓ labels.

Solution

For $n = 5$, ℓ can be 0, 1, 2, 3, or 4. Each subshell has $2\ell + 1$ orbitals. In tabular form:

n, ℓ	Label	No. of Orbitals
5, 0	5*s*	1
5, 1	5*p*	3
5, 2	5*d*	5
5, 3	5*f*	7
5, 4	5*g*	9

Wavefunctions for hydrogen-like systems, determined by quantum numbers, can be labeled with those quantum numbers. Therefore, it is common to see Ψ_{1s}, Ψ_{3d}, and so on.

As can be seen from Table 11.4, wavefunctions having a nonzero value for m_ℓ have an imaginary exponential function part. This means that the overall wavefunction is a complex function. In cases where completely real functions are desired, it is useful to define real wavefunctions as linear combinations of the complex wavefunctions, taking advantage of Euler's theorem. For example:

$$\begin{aligned} \Psi_{2p_x} &\equiv \frac{1}{\sqrt{2}}(\Psi_{2p_{+1}} + \Psi_{2p_{-1}}) \\ \Psi_{2p_y} &\equiv -\frac{i}{\sqrt{2}}(\Psi_{2p_{+1}} - \Psi_{2p_{-1}}) \end{aligned} \qquad \textbf{(11.67)}$$

The p wavefunctions defined like this are real, not complex, and so are easier to work with in many situations. Real wavefunctions for d, f, and other orbitals are defined similarly. These nonimaginary wavefunctions are *not* eigenfunctions of $\widehat{L}_z$ any longer, since they are composed of parts that have different eigenvalues of m_ℓ. They are still eigenfunctions of the energy and total angular momentum, however. (In fact, it is only *because* the original wavefunctions are degenerate that we are able to take linear combinations, like those in equation 11.67.)

The behavior of the wavefunctions in space raises some interesting points. Every s-type orbital has spherical symmetry, since there is no angular dependence in the wavefunction. Because the probability of an electron existing at any point in space is related to $|\Psi|^2$ or, in this case, $|R|^2$, the probability of an s electron existing in space is spherically symmetric also. Starting from the nucleus and moving out along a straight line, one can plot the probability of the electron having a certain value of r versus the radial distance r itself. Such a plot for Ψ_{1s} is shown in Figure 11.18. This plot shows the surprising conclusion that the radius of maximum probability occurs *at the nucleus,* that is, where $r = 0$.

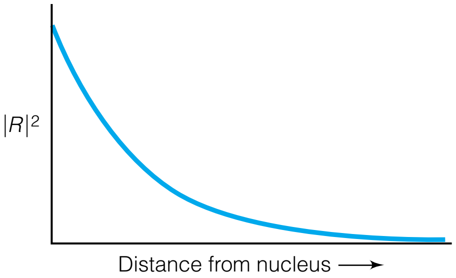


Figure 11.18 A plot of the square of the radial function of Ψ_{1s} versus distance from the nucleus for the hydrogen atom. It suggests that the electron has a maximum probability of existing at the nucleus.

This analysis is a little misleading. From a spherical polar viewpoint, there is very little volume of space close to the nucleus, because for all values of θ and ϕ a small value of r sweeps out a very tiny sphere. The total probability of the electron existing in such a small volume of space should be small. However, as the radius increases, the spherical volume swept out by the spherically symmetric wavefunction gets larger and larger, and one would expect an increase in probability that the electron will be located at greater distances from the nucleus.

Instead of considering the electron probability along a straight line out from the nucleus, consider the electron probability on a spherical surface around the nucleus, each spherical surface getting larger and larger. Mathematically, the spherical surface corresponds not to $|R|^2$, but $4\pi r^2|R|^2$. A plot of $4\pi r^2|R|^2$ versus r for Ψ_{1s} is shown in Figure 11.19. The probability starts at zero (a consequence of the "zero" volume at the nucleus), increases to a maximum, then decreases toward zero as the radius gets larger and approaches infinity. Quantum mechanics shows that an electron doesn't have a *specific* distance from the nucleus. Instead, it can have a range of distances having differing probabilities. It does have a most probable distance. It can be shown mathematically that the value of r at the most probable distance is

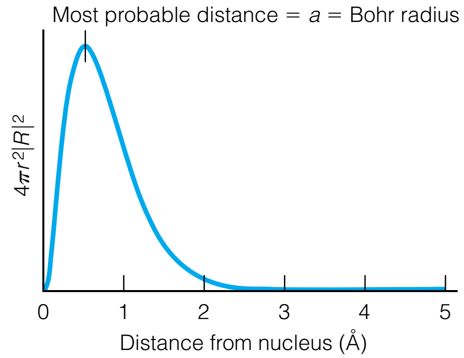


Figure 11.19 A plot of $4\pi r^2|R|^2$ for Ψ_{1s} versus distance from the nucleus. The $4\pi r^2$ contribution accounts for the spherical symmetry of the 1s wavefunction about the nucleus. By looking at the probability of existence in spherical shells rather than straight away from the nucleus, we get a more realistic picture of the expected behavior of an electron in a hydrogen atom.

$$r_{\max} = \frac{4\pi\hbar^2\epsilon_0}{\mu e^2} \equiv a \qquad \textbf{(11.68)}$$

$$a = 0.529 \text{ Å} \qquad \textbf{(11.69)}$$

where a is the same constant previously defined for the R functions. Since it is defined as a group of constants, a itself is a constant and has units of length (shown in equation 11.69 in units of Å). The constant a is called the *Bohr radius.* This most probable distance is *exactly the same distance* that an electron of Bohr's theory would have in its first orbit. Quantum mechanics does not constrain the distance of the electron from the nucleus as did Bohr's theory. But it does predict that the distance Bohr calculated for the electron in its lowest energy state is in fact the *most probable* distance of the electron from the nucleus. (It is sometimes written a_0, which is defined similarly but uses the mass of the electron instead of the reduced mass of the hydrogen atom. The difference is very slight.)

Example 11.24

a. What is the probability that an electron in the Ψ_{1s} orbital of hydrogen will be within a radius of 2.00 Å from the nucleus?
b. Calculate a similar probability, but now for an electron within 0.250 Å of a Be^{3+} nucleus.

Solution

a. For a normalized wavefunction, the probability P is equal to

$$P = \int_a^b \Psi^* \Psi \, d\tau$$

where a and b are the limits of the space being considered. For the hydrogen atom, this becomes the three-dimensional expression

$$P = \frac{1}{a^3 \pi} \int_0^{2\pi} d\phi \cdot \int_0^{\pi} \sin\theta \, d\theta \cdot \int_0^{2.00\text{ Å}} r^2 e^{-2r/a} \, dr$$

where the wavefunction in terms of the Bohr radius a has already been squared and the expression has been separated into three integrals. The two angular integrals we have done before, and the integral over r can be found in Appendix 1. The expression becomes

$$P = \frac{1}{a^3 \pi} \cdot 2\pi \cdot 2\left[e^{-2r/a}\left(\frac{-r^2 a}{2} - \frac{ra^2}{2} - \frac{a^3}{4} \right) \right] \Bigg|_0^{2.00\text{Å}}$$

If the value of a in units of angstroms, 0.529 Å, is used in the above expression, then the 2.00-Å limit can be used directly because the quantities are expressed in the same units. Substituting and evaluating the expression at the limits:

$$P = \frac{1}{(0.529\text{ Å})^3 \pi} \cdot 2\pi \cdot 2[(5.201 \times 10^{-4})(1.337841)\text{Å}^3 - (1)(-3.701 \times 10^{-2})\text{Å}^3]$$

Note that the Å^3 units cancel from the expression, and the probability is unitless (as it should be). Evaluating this expression, we find that

$$P = 0.981, \quad \text{or } 98.1\%$$

This example shows that the electron has a 98.1% probability of being within 2.00 Å, or slightly under 4 Bohr radii, from the nucleus. You might want to compare this with Figure 11.19, where the total probability is represented by the area under the curve. Finally, note that this implies a 1.9% chance that the electron is *farther* than 2.00 Å from the nucleus.

b. For the Be^{3+} nucleus, the solution to the problem is along similar lines but now the nuclear charge for the beryllium atom must be included explicitly. For $Z = 4$, the integrals being evaluated are

$$P = \frac{4^3}{a^3\pi}\int_0^{2\pi} d\phi \cdot \int_0^{\pi} \sin\theta \, d\theta \cdot \int_0^{0.250\text{Å}} r^2 e^{-8r/a}\, dr$$

Note that the upper limit on the r integral is now 0.250 Å. These expressions integrate to yield

$$P = \frac{64}{a^3\pi}\cdot 2\pi \cdot 2\left[e^{-8r/a}\left(\frac{-r^2a}{8} - \frac{ra^2}{32} - \frac{a^3}{256}\right)\right]\Bigg|_0^{0.250\text{Å}}$$

which yields

$$P = \frac{64}{(0.529\ \text{Å})^3\pi}\cdot 2\pi \cdot 2[(2.28 \times 10^{-2})(-0.00690)\text{Å}^3$$

$$- (1)(-5.78 \times 10^{-4})\text{Å}^3]$$

$$P = .728 \quad \text{or } 72.8\%$$

This is to be expected, since the larger nuclear charge pulls the single electron in closer to the nucleus. Therefore, there is a 72+% probability of finding a Ψ_{1s} electron within 0.250 Å of a Be^{3+} nucleus.

Radial probability plots for Ψ_{2s}, Ψ_{2p}, Ψ_{3s}, Ψ_{3p}, Ψ_{3d}, . . . are shown in Figure 11.20. For each wavefunction having quantum numbers n and ℓ, there are $n - \ell - 1$ points along a spherical radius where the probability of finding an electron becomes exactly zero. These points are *nodes.* Specifically, these are *radial nodes,* since we are considering the total electron probability at a spherical shell at each value of the radius.

Although s subshells are spherically symmetric, individual p, d, f, . . . subshells are not and do have angular dependence. There are several ways of conveying the angular dependence of subshells. One common way is to draw an outline within which the probability of the electron's appearance is 90%. It is easiest to use the real form of the wavefunctions to illustrate this behavior. Figure 11.21 shows the 90% boundary surfaces of real (that is, nonimaginary) p and d subshells of hydrogen. It is these angular distributions of the subshells that lend the "dumbbell" and "rosette" descriptions to the p and d orbitals.

There are several things to note about these plots. First, for each orbital, different axes are used to illustrate the plot, which means that the orbitals *point in different directions in space* even though they look very similar. Each section of the plots is labeled with a plus or a minus to indicate the sign of the wavefunction in that region. Next, for each p orbital there is one plane that is tangent to all electron probability. As an example, for the p_z orbital, the xy plane is the plane of exactly zero electron probability. For the p_x orbital, the yz plane has zero electron probability. For the d orbitals, there are two planes where the electron probability is zero. These are examples of *angular nodes* (also called nodal planes or nodal surfaces). Figure 11.22 shows some of the angular nodes for p and d orbitals. For the d_{z^2} orbital, the nodal surface is a two-dimensional cone. For quantum number ℓ, there will be ℓ angular nodes. Combining angular nodes with radial nodes, there will be a total of $n - 1$ nodes (both radial and angular) for any wavefunction $\Psi_{n,\ell}$.

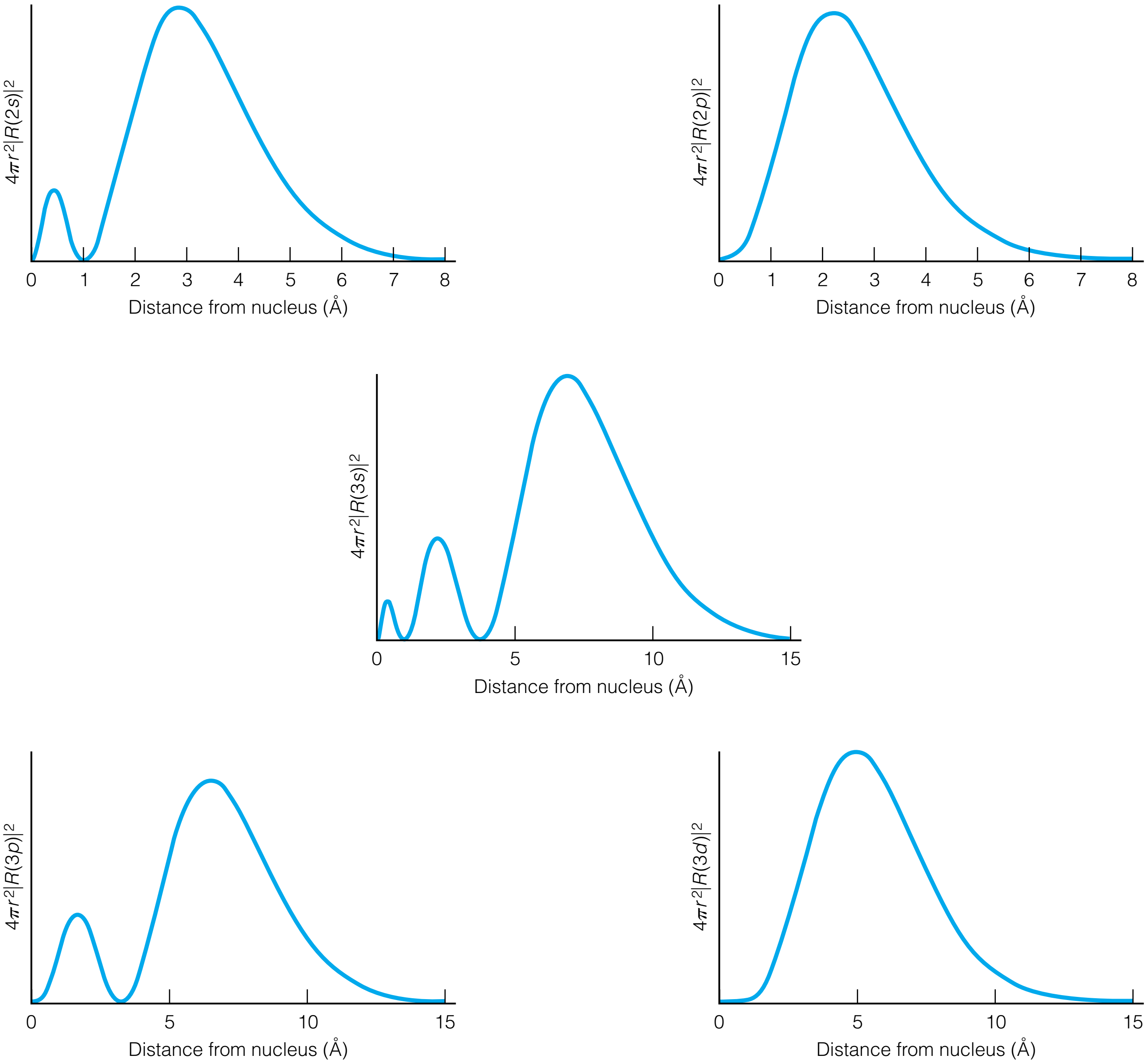


Figure 11.20 Plots of $4\pi r^2|R|^2$ versus distance for other hydrogen atom wavefunctions, as labeled. There is a simple relationship between the quantum numbers and the number of radial nodes.

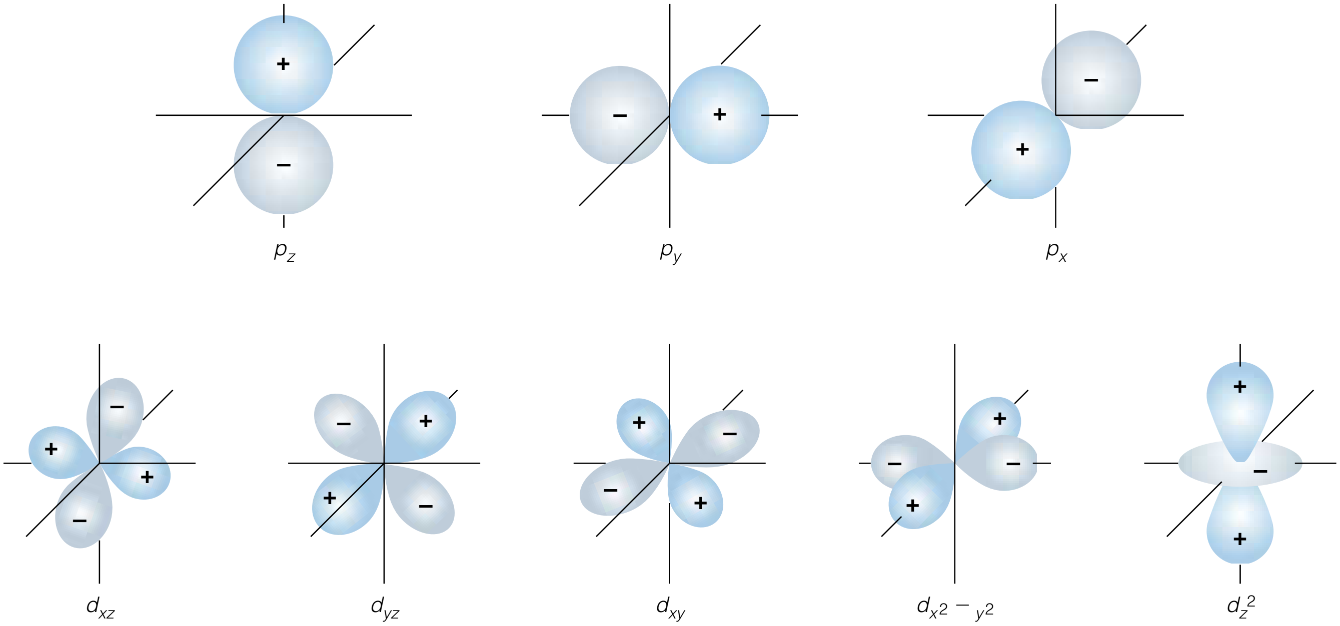


Figure 11.21 The 90% boundary plots for the real forms of *p* and *d* wavefunctions. The specific label on the *p* or *d* orbital depends on the direction the orbital takes in 3-D space.

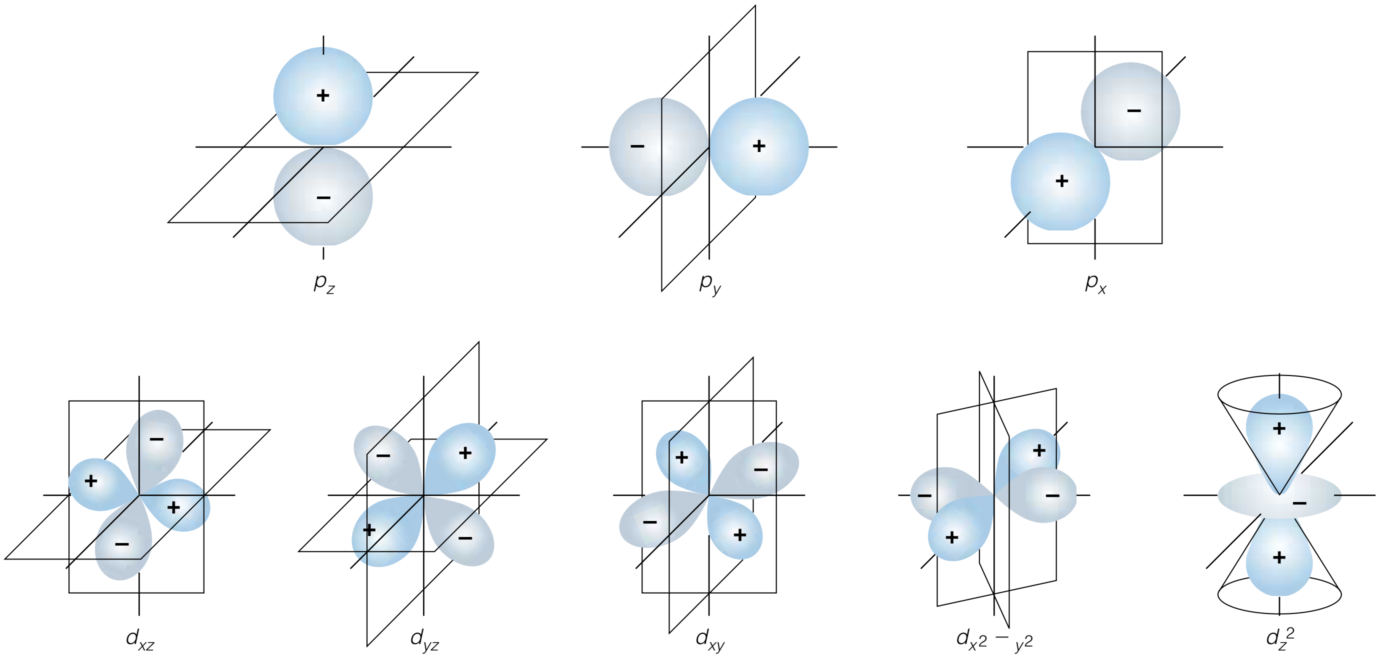


Figure 11.22 Nodal planes for *p* and *d* orbitals. Each *p* orbital has one nodal plane. Each *d* orbital has two nodal planes. For the d_{z^2} orbital, the nodal planes are represented by a single conical surface.

Example 11.25

a. What is the average value of the total angular momentum for Ψ_{3p} for the hydrogen atom?
b. Is there an easier way to determine this value?

Solution

a. The *square* of the total angular momentum is defined, so we will assume that the average angular momentum is the square root of the squared angular momentum. Therefore, we need to find

$$\langle L \rangle = \sqrt{\langle L^2 \rangle}$$

To do this, we need to determine the average value $\langle L^2 \rangle$. This is done with the following expression:

$$\langle L^2 \rangle = \int \Psi_{3p}^* \hat{L}^2 \Psi_{3p} \, d\tau$$

It might seem at first that we may have to use the long, complete form of Ψ_{3p} and the long, complete form of $\hat{L}^2$; we don't, though. Since Ψ_{3p} is an eigenfunction of $\hat{L}^2$, we can substitute the eigenvalue for the operator in the integral above. Since the eigenvalue is $\ell(\ell + 1)\hbar^2$, the integral above becomes

$$\langle L^2 \rangle = \int \Psi_{3p}^* [\ell(\ell + 1)\hbar^2] \, \Psi_{3p} \, d\tau$$

where the constants are multiplied with the wavefunctions instead of any function-changing operation occurring. Multiplicative constants are moved outside the integral sign, so the above expression becomes

$$\langle L^2 \rangle = \ell(\ell + 1)\hbar^2 \int \Psi_{3p}^* \Psi_{3p} \, d\tau$$

The wavefunction is normalized, so the integral is simply 1. Therefore,

$$\langle L^2 \rangle = \ell(\ell + 1)\hbar^2$$

and using the value of $\ell = 1$ for a p orbital, we can determine the average value of the total angular momentum $\langle L \rangle$ as

$$\langle L \rangle = \sqrt{\langle L^2 \rangle} = \sqrt{\ell(\ell + 1)\hbar^2} = \sqrt{2}\hbar = 1.491 \times 10^{-34} \text{ J·s}$$

b. The easier way is to realize that L^2 is a quantized observable for the $3p$ wavefunction of a hydrogen atom. The average value is equal to the quantized value. This will not always be the case for average values (see exercises 11.58 or 11.60, for example).

11.12 Summary

With the solution of the hydrogen atom, the list of analytically solvable systems to be considered here is complete. Planck's quantum theory of light described blackbody radiation, and now the simplicity of the spectrum of the hydrogen (and hydrogen-like ions) is adequately explained by quantum mechanics. We will find in the next chapter that although an exact *analytic* understanding of the behavior of electrons in larger atoms is not forthcoming, quantum mechanics does provide the tools for a numerical solution to larger systems, like molecules (for smaller molecules in practice, and for larger molecules at least in theory). Because this is far more than the classical theories of chemistry and physics could provide, quantum mechanics is accepted as the superior theory of the behavior of matter at the electronic level. The postulates of quantum mechanics allow for some seemingly unusual and unexpected behavior—like tunneling, quantized angular momenta, and “fuzzy” electron orbitals. But so far, the predictions of quantum mechanics have been borne out when examined experimentally. That is the true test of a theory.

EXERCISES FOR CHAPTER 11

11.2 Classical Harmonic Oscillator

11.1. Convert 3.558 mdyn/Å into units of N/m.

11.2. A swinging pendulum has a frequency of 0.277 Hz and a mass of 500.0 kg. Calculate the force constant for this harmonic oscillator.

11.3. An object having mass m at some height above the ground h has a gravitational potential energy of mgh, where g is the acceleration due to gravity (~ 9.8 m/s^2). Explain why objects moving back and forth under the influence of gravity (like a clock's pendulum) can be treated as harmonic oscillators. (*Hint:* see equation 11.1.)

11.3 Quantum-Mechanical Harmonic Oscillator

11.4. In equation 11.6, in order to properly subtract the two terms in parentheses on the left, they must have the same units overall. Verify that $2mE/\hbar^2$ and $\alpha^2 x^2$ have the same units. Use standard SI units for x (position/distance). Do the same for the two terms in parentheses in equation 11.11.

11.5. Verify that the three substitutions mentioned in the text yield equation 11.6.

11.6. Verify that the second derivative of Ψ given by equation 11.8 gives equation 11.9.

11.7. Derive equation 11.16 from the equation immediately preceding it.

11.8. Show that the energy separation between *any* two adjacent energy levels for an ideal harmonic oscillator is $h\nu$, where ν is the classical frequency of the oscillator.

11.9. **(a)** For a pendulum having a classical frequency of 1.00 s^{-1}, what is the energy difference in J between quantized energy levels? **(b)** Calculate the wavelength of light that must be absorbed in order for the pendulum to go from one level to another. **(c)** Can you determine in what region of the electromagnetic spectrum such a wavelength belongs? **(d)** Comment on your results for parts a and b based on your knowledge of the state of science in the early twentieth century. Why wasn't the quantum mechanical behavior of nature noticed?

11.10. **(a)** A hydrogen atom bonded to a surface is acting as a harmonic oscillator with a classical frequency of 6.000×10^{13} s^{-1}. What is the energy difference in J between quantized energy levels? **(b)** Calculate the wavelength of light that must be absorbed in order for the hydrogen atom to go from one level to another. **(c)** Can you determine in what region of the electromagnetic spectrum such a wavelength belongs? **(d)** Comment on your results for parts a and b based on your knowledge of the state of science in the early twentieth century.

11.11. The O–H bond in water vibrates at a frequency of 3650 cm^{-1}. What wavelength and frequency (in s^{-1}) of light would be required to change the vibrational quantum number from $n = 0$ to $n = 4$, assuming O–H acts as a harmonic oscillator?

11.4 Harmonic Oscillator Wavefunctions

11.12. Show that Ψ_2 and Ψ_3 for the harmonic oscillator are orthogonal.

11.13. Substitute Ψ_1 into the complete expression for the Hamiltonian operator of an ideal harmonic oscillator and show that $E = \frac{3}{2}h\nu$.

11.14. Calculate $\langle p_x \rangle$ for Ψ_0 and Ψ_1 for a harmonic oscillator. Do the values you calculate make sense?

11.15. Use the expression for Ψ_1 in equations 11.17 and normalize the wavefunction. Use the integral defined for the Hermite polynomials in Table 11.2. Compare your answer with the wavefunction defined by equation 11.19.

11.16. Simply using arguments based on odd or even functions, determine whether the following integrals involving harmonic oscillator wavefunctions are identically zero, are not identically zero, or are indeterminate. If indeterminate, state why.

(a) $\int_{-\infty}^{+\infty} \Psi_1^* \Psi_2 \, dx$ **(b)** $\int_{-\infty}^{+\infty} \Psi_1^* \, \hat{x} \, \Psi_1 \, dx$

(c) $\int_{-\infty}^{+\infty} \Psi_1^* \hat{x}^2 \Psi_1 \, dx$, where $\hat{x}^2 = \hat{x} \cdot \hat{x}$

(d) $\int_{-\infty}^{+\infty} \Psi_1^* \Psi_3 \, dx$ **(e)** $\int \Psi_3^* \Psi_3 \, dx$

(f) $\int_{-\infty}^{+\infty} \Psi_1^* \hat{V} \Psi_1 \, dx$, where $\hat{V}$ is some undefined potential energy function.

11.17. Determine the value(s) of x for the classical turning point of a harmonic oscillator in terms of k and n. There may be other constants in the expression you derive.

11.5 Reduced Mass

11.18. Compare the mass of the electron, m_e, with **(a)** the reduced mass of a hydrogen atom; **(b)** the reduced mass of a deuterium atom (deuterium = ^{2}H); **(c)** the reduced mass of a carbon-12 atom having a +5 charge, that is, C^{5+}. Suggest a conclusion to the trend presented by parts a–c.

11.19. Reduced mass is not reserved only for atomic systems. A solar system or a planet/satellite system, for example, can have its behavior described by first determining its reduced mass. If the mass of Earth is 2.435×10^{24} kg and that of the moon is 2.995×10^{22} kg, what is the reduced mass of the Earth-moon system? (This is not to imply any support of a planetary model for atoms!)

11.20. **(a)** Calculate the expected harmonic-oscillator frequency of vibration for carbon monoxide, CO, if the force constant is 1902 N/m. **(b)** What is the expected frequency of ^{13}CO, assuming the force constant remains the same?

11.21. An O–H bond has a frequency of 3650 cm^{-1}. Using equation 11.27 twice, set up a ratio and determine the expected frequency of an O–D bond, without calculating the force constant. D = deuterium (^{2}H). Assume that the force constant remains the same.

11.6 2-D Rotations

11.22. Why can't the quantized values of the 2-D angular momentum be used to determine the mass of a rotating system, like classical angular momentum can?

11.23. Show that Ψ_3 of 2-D rotational motion has the same normalization constant as Ψ_{13} by normalizing both wavefunctions.

11.24. What are the energies and angular momenta of the first five energy levels of benzene in the 2-D rotational motion approximation? Use the mass of the electron and a radius of 1.51 Å to determine I.

11.25. A 25-kg child is on a merry-go-round/calliope, going around and around in a large circle that has a radius of 8 meters. The child has an angular momentum of 600. kg·m^2/s. **(a)** From these facts, estimate the approximate quantum number for the angular momentum the child has. **(b)** Estimate the quantized amount of energy the child has in this situation. How does this compare to the child's classical energy? What principle does this illustrate?

11.26. Using Euler's identity, rewrite the first four 2-D rotational wavefunctions in terms of sine and cosine.

11.27. **(a)** Using the expression for the energy of a 2-D rigid rotor, construct the expression for the energy difference between two adjacent levels, $E(m + 1) - E(m)$. **(b)** For HCl, $E(1) - E(0) = 20.7\ \text{cm}^{-1}$. Calculate $E(2) - E(1)$, assuming HCl acts as a 2-D rigid rotor. **(c)** This energy difference is determined experimentally as 41.4 cm^{-1}. How good would you say a 2-D model is for this system?

11.28. Derive equation 11.35 from 11.34.

11.7 & 11.8 3-D Rotations

11.29. Use trigonometry to verify the relationships between the Cartesian and spherical polar coordinates as given in equation 11.40.

11.30. Why can't the square root of equation 11.45 be taken analytically? (*Hint:* consider how you would have to take the square root of the right side of the equation. Can it be done?)

11.31. For both 2-D and 3-D rotations, the radius of the particle's motion is kept constant. Consider a nonzero, constant potential energy acting on the particle. Show that the form of the Schrödinger equation in equation 11.46 would be equivalent to its form if V were identically zero. (*Hint:* use the idea that $E_{\text{new}} = E - V$.)

11.32. Can you evaluate $\langle r \rangle$ for the spherical harmonic Y^{2}_{-2}? Why or why not?

11.33. Using the complete form of $\Psi_{3,-2}$ (where $\ell = 3$ and $m_\ell = -2$) for 3-D rotations (get the Legendre polynomial from Table 11.3) and the complete forms of the operators, evaluate the eigenvalues of **(a)** L^2, **(b)** L_z, **(c)** E. Do not use the analytic expressions for the observables. Instead, operate on $\Psi_{3,-2}$ with the appropriate operators and see that you do get the proper eigenvalue equation. From the eigenvalue equation, determine the value of the observable.

11.34. A 3-D rotational wavefunction has the quantum number ℓ equal to 2 and a moment of inertia of 4.445×10^{-47} kg·m^2. What are the possible numerical values of **(a)** the energy; **(b)** the total angular momentum; **(c)** the z component of the total angular momentum?

11.35. **(a)** Using the expression for the energy of a 3-D rigid rotor, construct the expression for the energy difference between two adjacent levels, $E(\ell + 1) - E(\ell)$.

(b) For HCl, $E(1) - E(0) = 20.7\ \text{cm}^{-1}$. Calculate $E(2) - E(1)$, assuming HCl acts as a 3-D rigid rotor.

(c) This energy difference is determined experimentally as 41.4 cm^{-1}. How good would you say a 3-D model is for this system?

11.36. See Example 11.17, regarding the "spherical" C_{60} molecule. Assuming the electrons in this molecule are experiencing 3-D rotations, calculate the wavelength of light necessary to cause a transition from state $\ell = 5$ to $\ell = 6$ and from $\ell = 7$ to $\ell = 8$. Compare your answers with experimentally measured absorptions at wavelengths of 328 and 256 nm. How good is this model for describing C_{60}'s electronic absorptions?

11.37. In exercise 11.36 regarding C_{60}, what are the numerical values of the total angular momenta of the electron for each state having quantum number ℓ? What are the z components of the angular momentum for each state?

11.38. Draw graphical representations (see Figure 11.15) of the possible values for ℓ and m_ℓ for the first four energy levels of the 3-D rigid rotor. What are the degeneracies of each state?

11.39. What is a physical explanation of the difference between a particle having the 3-D rotational wavefunction $\Psi_{3,2}$ and an identical particle having the wavefunction $\Psi_{3,-2}$?

11.9, 11.10, & 11.11 Hydrogen-Like Atoms

11.40. List the charges on hydrogen-like atoms whose nuclei are of the following elements. **(a)** lithium, **(b)** carbon, **(c)** iron, **(d)** samarium, **(e)** xenon, **(f)** francium, **(g)** uranium, **(h)** seaborgium

11.41. Calculate the electrostatic potential energy V between an electron and a proton if the electron is at a distance of 1 Bohr radius (0.529 Å) from the proton. Be careful that the correct units are used!

11.42. Using Newton's law of gravity and the relationship between force and potential energy, the gravitational potential energy can be written as

$$V = -G\frac{m_1 m_2}{r}$$

Use the masses of the electron and the proton and the gravitational constant $G = 6.673 \times 10^{-11}\ \text{N·m}^2/\text{kg}^2$ to show that the gravitational potential energy is negligible compared to the electrostatic potential energy at a distance of 1 Bohr radius.

11.43. Show that for constant r and $V = 0$, equation 11.56 becomes equation 11.46. (*Hint:* you will have to apply the chain rule of differentiation to the derivatives in the second term of equation 11.56.)

11.44. Calculate the difference between the Bohr radius defined as a and the Bohr radius defined as a_0.

11.45. To four significant figures, the first four lines in the Balmer series in the hydrogen atom ($n_2 = 2$) spectrum appear at 656.5, 486.3, 434.2, and 410.3 nm. **(a)** From these numbers, calculate an average value of R_H, the Rydberg constant. **(b)** At what wavelengths would similar transitions appear for He^+?

11.46. What would the wavelengths of the Balmer series for deuterium be?

11.47. Construct an energy level diagram showing all orbitals for the hydrogen atom up to $n = 5$, labeling each orbital with its appropriate quantum numbers. How many different orbitals are in each shell?

11.48. What are the values of E, L, and L_z for an F^{8+} atom whose electron has the following wavefunctions, listed as Ψ_{n,ℓ,m_ℓ}? **(a)** $\Psi_{1,0,0}$ **(b)** $\Psi_{3,2,2}$ **(c)** $\Psi_{2,1,-1}$ **(d)** $\Psi_{9,6,-3}$.

11.49. Why does the wavefunction $\Psi_{4,4,0}$ not exist? Similarly, why does a $3f$ subshell not exist? (See exercise 11.48 for notation definition.)

11.50. Calculate the total electronic energy of a mole of hydrogen atoms. Calculate the total electronic energy of a mole of He^+ atoms. What accounts for the difference in the two total energies?

11.51. What is the probability of finding an electron in the $1s$ orbital within 0.1 Å of a hydrogen nucleus?

11.52. What is the probability of finding an electron in the $1s$ orbital within 0.1 Å of an Ne^{9+} nucleus? Compare your answer to the answer to exercise 11.51 and justify the difference.

11.53. State how many radial, angular, and total nodes are in each of the following hydrogen-like wavefunctions. **(a)** Ψ_{2s} **(b)** Ψ_{3s} **(c)** Ψ_{3p} **(d)** Ψ_{4f} **(e)** Ψ_{6g} **(f)** Ψ_{7s}

11.54. Illustrate that the hydrogen wavefunctions are orthogonal by evaluating $\int \Psi_{2s}^{*} \Psi_{1s}\, d\tau$ over all space.

11.55. Verify the specific value of a, the Bohr radius, by using the values of the various constants and evaluating equation 11.68.

11.56. Show that r_{max} is given by equation 11.68 for Ψ_{1s}. Take the derivative of $4\pi r^2 \Psi^2$ with respect to r, set it equal to zero, and solve for r.

11.57. Use the forms of the wavefunctions in Table 11.4 to determine the explicit forms for the 2_{p_x} and 2_{p_y} nonimaginary wavefunctions.

11.58. Evaluate $\langle L_z \rangle$ for 3_{p_x}. Compare it to the answer in Example 11.25, and explain the difference in the answers.

11.59. Using equations 11.67 as an example, what would the combinations for the five real $3d$ wavefunctions be? Use Table 11.4 to assist you.

11.60. Evaluate $\langle r \rangle$ for Ψ_{1s} (assume that the operator $\hat{r}$ is defined as "multiplication by the coordinate r"). Why does $\langle r \rangle$ not equal 0.529 Å for Ψ_{1s}? In this case, $d\tau = 4\pi r^2\, dr$.

Symbolic Math Exercises

11.61. Graph the first five wavefunctions for the harmonic oscillators and their probabilities. Superimpose these graphs on the potential energy function for a harmonic oscillator and numerically determine the x values of the classical turning points. What is the probability that an oscillator will exist beyond the classical turning points? Do plots of the probability begin to show a distribution as expected by the correspondence principle?

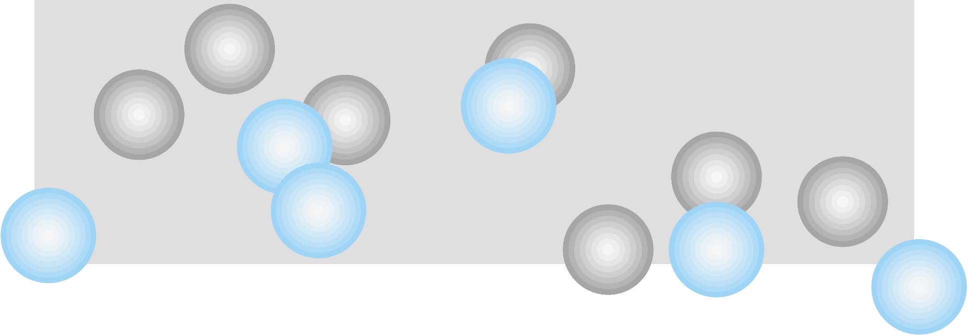
11.62. Construct three-dimensional plots of the first three families of spherical harmonics. Can you identify the values of θ and ϕ that correspond to nodes?

11.63. Set up and evaluate numerically the integral that shows that Y_1^1 and Y_{-1}^1 are orthogonal.

11.64. Plot the 90% surfaces of the hydrogen atom $2s$ and $2p$ angular wavefunctions in 3-D space. Can you identify nodes in your graphic?

12

Atoms and Molecules



WE HAVE SEEN HOW QUANTUM MECHANICS provides tools for understanding some simple systems, up to and including the hydrogen atom itself. An understanding of the H atom is a crucial point because it is *real,* not a model system. Quantum mechanics showed that it can describe the hydrogen atom like Bohr's theory did. It also describes other model systems that have applications in the real world. (Recall that all of the model systems—particle-in-a-box, 2-D and 3-D rigid rotors, harmonic oscillators—could be *applied* to real systems even if the real systems themselves weren't exactly ideal.) As such, quantum mechanics is more applicable than Bohr's theory and can be considered "better." We will conclude our development of quantum mechanics by seeing how it applies to more complicated systems: other atoms and even molecules. What we will find is that explicit, analytic solutions to these systems are not possible, but quantum mechanics does supply the tools for understanding these systems nonetheless.

12.1 Synopsis

In this chapter, we will consider one more property of the electron, which is called spin. Spin has dramatic consequences for the structure of matter, consequences that could not have been considered by the standards of classical mechanics. We will see that an exact, analytic solution for an atom as simple as helium is not possible, and so the Schrödinger equation cannot be solved analytically for larger atoms or molecules. But there are two tools for studying larger systems to any degree of accuracy: perturbation theory and variational theory. Each tool has its advantages, and both of them are used today to study atoms and molecules and their reactions.

Finally, we will consider in a simple way how quantum mechanics considers a molecular system. Molecules can get very complicated. However, we *can* apply quantum mechanics to molecules. We will finish this chapter with an introduction to molecular orbitals and how they are defined for a very simple molecule, H_2^+. Simple as this system is, it paves the way for other molecules.

12.2 Spin

Not long before quantum mechanics was developed, an important experimental observation was made. In 1922, Otto Stern and W. Gerlach attempted to measure the magnetic moment of the silver atom. They passed vaporized silver atoms through a magnetic field and recorded the pattern that the beam of atoms made after it passed through the magnetic field. Surprisingly, the beam split into two parts. The experiment is illustrated in Figure 12.1.

Attempts to explain this in terms of the Bohr theory and quantized angular momentum of electrons in their orbits failed. Finally, in 1925, George Uhlenbeck and Samuel Goudsmit proposed that this result could be explained if it was assumed that the electron had its *own* angular momentum. This angular momentum was an intrinsic property of the electron itself and not a consequence of any motion of the electron. In order to explain the experimental results, Uhlenbeck and Goudsmit proposed that components of the intrinsic angular momentum, called *spin angular momentum,* had quantized values of either $+\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$. (Recall that h has units of angular momentum.)

Since that proposal, it has become understood that all electrons have an intrinsic angular momentum called *spin.* Although commonly compared to the spinning of a top, the spin angular momentum of an electron is not due to any rotation about the axis of the particle. Indeed, it would be impossible for us to determine that an electron is actually spinning. Spin is a property of a particle's very existence. This property behaves as if it were an angular momentum, so for all intents and purposes it is considered an angular momentum.

Like the angular momentum of an electron in its orbit, there are two measurables for spin that can be observed simultaneously: the square of the total spin and the z component of the spin. Because spin is an angular momentum, there are eigenvalue equations for the spin observables that are the same as for $\widehat{L}^2$ and $\widehat{L}_z$, except we use the operators $\widehat{S}^2$ and $\widehat{S}_z$ to indicate the spin observables. We also introduce the quantum numbers s and m_s to represent the quantized values of the spin of the particles. (Do not confuse s, the symbol for the

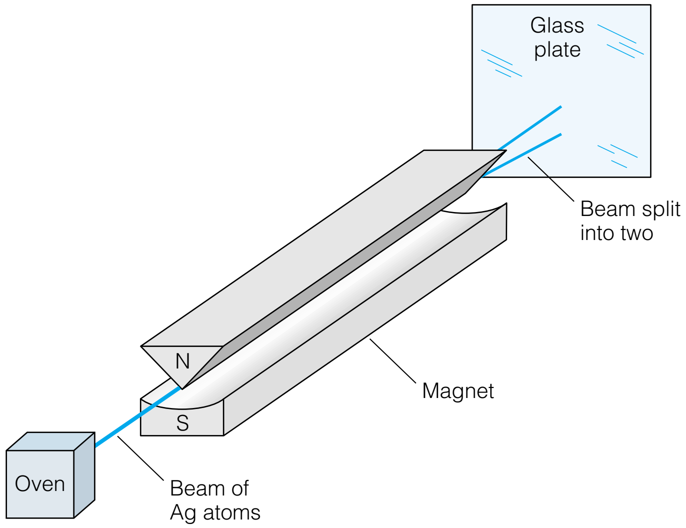


Figure 12.1 A diagram of the Stern-Gerlach experiment. A beam of silver atoms passed through a magnetic field splits into two separate beams. This finding was used to propose the existence of spin on the electron.

spin angular momentum, with s, an orbital that has $\ell = 0$.) The eigenvalue equations are therefore

$$\hat{S}^2\Psi = s(s+1)\hbar^2\Psi \tag{12.1}$$

$$S_z\Psi = m_s\hbar\Psi \tag{12.2}$$

The values of the allowed quantum numbers s and m_s are more restricted than for ℓ and m_ℓ. All electrons have a value of $s = \frac{1}{2}$. The value of s, it turns out, is a characteristic of a type of subatomic particle, and all electrons have the same value for their s quantum number. For the possible values of the z component of the spin, there is a similar relationship to the possible values of m_ℓ and ℓ: m_s goes from $-s$ to $+s$ in integral steps, so m_s can equal $-\frac{1}{2}$ or $+\frac{1}{2}$. Thus, there is only one possible value of s for electrons, and two possible values for m_s.

Spin also has no classical counterpart. Nothing in classical mechanics predicts or explains the existence of a property we call spin. Even quantum mechanics, at first, did not provide any justification for spin. It wasn't until 1928 when Paul A. M. Dirac incorporated relativity theory into the Schrödinger equation that spin appeared as a natural theoretical prediction of quantum mechanics. The incorporation of relativity into quantum mechanics was one of the final major advances in the development of the theory of quantum mechanics. Among other things, it led to the prediction of antimatter, whose existence was verified experimentally by Carl Anderson (with the discovery of the positron) in 1932.

Example 12.1

What is the value, in J·s, of the spin of an electron? Compare this to the value of the angular momentum for an electron in s and p orbitals of an H-like atom.

Solution

The value of the spin angular momentum of an electron is determined by using equation 12.1. We must recognize that the operator is the square of the total spin, and to find the value for spin we will have to take a square root. We get

$$\text{spin} = \sqrt{s(s+1)\hbar^2} = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)\left(\frac{6.626\times10^{-34}\,\text{J·s}}{2\pi}\right)^2}$$

$$= 9.133 \times 10^{-35}\ \text{J·s}$$

The angular momentum of an electron in an s orbital is zero, since $\ell = 0$ for an electron in an s orbital. In a p orbital, $\ell = 1$, so the angular momentum is

$$\sqrt{\ell(\ell+1)}\hbar = \sqrt{1\cdot 2}\,\frac{6.626\times10^{-34}\ \text{J·s}}{2\pi} = 1.491\times10^{-34}\ \text{J}\cdot\text{s}$$

which is almost twice as great as the spin. The magnitude of the spin angular momentum is not much smaller than the angular momentum of an electron in its orbit. Its effects, therefore, cannot be ignored.

The existence of an intrinsic angular momentum requires some additional specificity when referring to angular momenta of electrons. One must now differentiate between *orbital* angular momentum and *spin* angular momentum. Both observables are angular momenta, but they arise from different properties of the electron: one from its motion about a nucleus, the other from its very existence.

The spin angular momentum of an electron can have only certain specific values. Spin is *quantized*. Like the z component of orbital angular momentum, m_s has $2s + 1$ possible values. In the case of the electron, $s = \frac{1}{2}$, so the only possible values of m_s are $-\frac{1}{2}$ and $+\frac{1}{2}$. The specification of an electron's spin therefore represents two other quantum numbers that can be used to label the state of that electron. In practice, however, it is convenient to not specify s, since it is always $\frac{1}{2}$ for electrons. This gives us a total of four quantum numbers: the principal quantum number n, the orbital angular momentum quantum number ℓ, the orbital angular momentum z component m_ℓ, and the spin angular momentum (z component) m_s. These are the only four quantum numbers needed to specify the complete state of an electron.

Example 12.2

List all possible combinations of all four quantum numbers for an electron in the $2p$ orbital of a hydrogen atom.

Solution

In tabular form, the possible combinations are

Symbol	Possible values		
n	2		
ℓ	1		
m_ℓ	-1	0	1
m_s	$+\frac{1}{2}$ or $-\frac{1}{2}$	$+\frac{1}{2}$ or $-\frac{1}{2}$	$+\frac{1}{2}$ or $-\frac{1}{2}$

There are a total of six possible combinations of the four quantum numbers for this case.

Although not considered until now, the m_s of the electron in a hydrogen atom is either $+\frac{1}{2}$ or $-\frac{1}{2}$. A fascinating astronomical consequence of spin is the fact that an electron in hydrogen has a slightly different energy depending on the relative spin orientations of the electron and the proton in the nucleus. (A proton also has a characteristic spin quantum number of $\frac{1}{2}$.) If an electron in a hydrogen atom changes its spin, there is a concurrent energy change that is equivalent to light having a frequency of 1420.40575 MHz, or a wavenumber of about 21 cm^{-1}, as shown in Figure 12.2. Because of the pervasiveness of hydrogen in space, this "21-cm^{-1} radiation" is important for radio astronomers who are studying the structure of the universe.

Finally, since spin is part of the properties of an electron, its observable values should be determined from the electron's wavefunction. That is, there should be a spin wavefunction part of the overall Ψ. A discussion of the exact form of the spin part of a wavefunction is beyond our scope here. However, since there is only one possible observable value of the total spin ($s = \frac{1}{2}$) and only two possible values of the z component of the spin ($m_s = +\frac{1}{2}$ or $-\frac{1}{2}$), it is typical to represent the spin part of the wavefunction by the Greek letters α and β, depending on whether the quantum number m_s is $+\frac{1}{2}$ or $-\frac{1}{2}$, respectively.

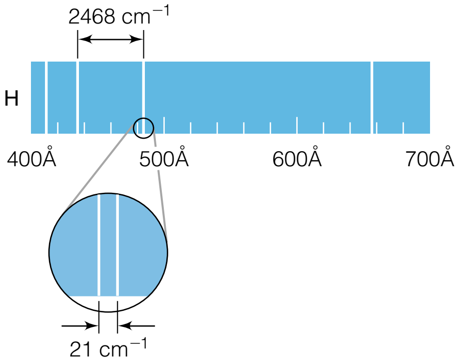


Figure 12.2 A very high resolution spectrum of the hydrogen atom shows a tiny splitting due to the spin on the electron. This splitting is caused by the electron spin interacting with the nuclear spin of the hydrogen atom's nucleus (a proton).

Spin is unaffected by any other property or observable of the electron, and the spin component of a one-electron wavefunction is separable from the spatial part of the wavefunction. Like the three parts of the hydrogen atom's electronic wavefunction, the spin function multiplies the rest of Ψ. So for example, the complete wavefunctions for an electron in a hydrogen atom are

$$\Psi = R_{n,\ell} \cdot \Theta_{\ell,m_\ell} \cdot \phi_{m_\ell} \cdot \alpha$$

for an electron having m_s of $+\frac{1}{2}$. A similar wavefunction, in terms of β, can be written for an electron having $m_s = -\frac{1}{2}$.

12.3 The Helium Atom

In the previous chapter, it was shown how quantum mechanics provides an exact, analytic solution to the Schrödinger equation when applied to the hydrogen atom. Even the existence of spin, discussed in the last section, does not alter this solution (it only adds a little more complexity to the solution, a complexity we will not consider further here). The next largest atom is the helium atom, He. It has a nuclear charge of 2+, and it has two electrons about the nucleus. The helium atom is illustrated in Figure 12.3, along with some of the coordinates used to describe the positions of the subatomic particles. Implicit in the following discussion is the idea that both electrons of helium will occupy the lowest possible energy state.

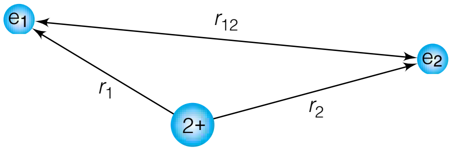


Figure 12.3 Definitions of the radial coordinates for the helium atom.

In order to properly write the complete form of the Schrödinger equation for helium, it is important to understand the sources of the kinetic and potential energy in the atom. Assuming only electronic motion with respect to a motionless nucleus, kinetic energy comes from the motion of the two electrons. It is assumed that the kinetic energy part of the Hamiltonian operator is the same for the two electrons and that the total kinetic energy is the sum of the two individual parts. To simplify the Hamiltonian, we will use the symbol ∇^2, called del-squared, to indicate the three-dimensional second derivative operator:

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{12.3}$$

This definition makes the Schrödinger equation look less complicated. ∇^2 is also called the *Laplacian operator.* It is important to remember, however, that del-squared represents a sum of three separate derivatives. The kinetic energy part of the Hamiltonian can be written as

$$-\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{\hbar^2}{2\mu}\nabla_2^2$$

where ∇_1^2 is the three-dimensional second derivative for electron 1, and ∇_2^2 is the three-dimensional second derivative for electron 2.

The potential energy of the helium atom has three parts, all coulombic in nature: there is an attraction between electron 1 and the nucleus, an attraction between electron 2 and the nucleus, and a *repulsion* between electron 1 and electron 2 (since they are both negatively charged). Each part depends on the distance between the particles involved; the distances are labeled r_1, r_2, and r_{12} as illustrated in Figure 12.3. Respectively, the potential energy part of the Hamiltonian is thus

$$\hat{V} = -\frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

where the other variables have been defined in the previous chapter. The 2 in the numerator of each of the first two terms is due to the 2+ charge on the helium nucleus. The first two terms are negative, indicating an attraction, and the final term is positive, indicating a repulsion. The complete Hamiltonian operator for the helium atom is

$$\widehat{H} = -\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{12.4}$$

This means that for the helium atom, the Schrödinger equation to be solved is

$$\left(-\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 \mathrm{r}_{12}}\right)\Psi = E_{\mathrm{tot}}\Psi \tag{12.5}$$

where E_{tot} represents the total electronic energy of a helium atom.

The Hamiltonian (and thus the Schrödinger equation) can be rearranged by grouping together the two terms (one kinetic, one potential) that deal with electron 1 only and also grouping together the two terms that deal with electron 2 only:

$$\widehat{H} = \left(-\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1}\right) + \left(-\frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2}\right) + \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{12.6}$$

This way, the Hamiltonian resembles two separate one-electron Hamiltonians added together. This suggests that perhaps the helium atom wavefunction is simply a combination of two hydrogen-like wavefunctions. Perhaps a sort of "separation of electrons" approach will allow us to solve the Schrödinger equation for helium.

The problem is with the last term: $e^2/4\pi\epsilon_0 r_{12}$. It contains a term, r_{12}, that depends on the positions of *both* of the electrons. It does not belong only with the terms for just electron 1, nor does it belong only with the terms for just electron 2. Because this last term cannot be separated into parts involving only one electron at a time, the complete Hamiltonian operator is *not separable* and it cannot be solved by separation into smaller, one-electron pieces. In order for the Schrödinger equation for the helium atom to be solved analytically, it either must be solved completely or not at all.

To date, there is no known analytic solution to the second-order differential Schrödinger equation for the helium atom. This does not mean that there is no solution, or that wavefunctions do not exist. It simply means that we know of no *mathematical* function that satisfies the differential equation. In fact, for atoms and molecules that have more than one electron, the lack of separability leads directly to the fact that *there are no known analytical solutions to any atom larger than hydrogen.* Again, this does not mean that the wavefunctions do not exist. It simply means that we must use other methods to understand the behavior of the electrons in such systems. (It has been proven mathematically that there is no analytic solution to the so-called three-body problem, as the He atom can be described. Therefore, we must approach multi-electron systems differently.)

Nor should this lack be taken as a failure of quantum mechanics. In this text, we can only scratch the surface of the tools that quantum mechanics provides. Quantum mechanics does provide tools to understand such systems. Atoms and molecules having more than one electron can be studied and understood by applying such tools to more and more exacting detail. The level of detail depends on the time, resources, and patience of the person applying the tools. In theory, one can determine energies and momenta and other observables to the same level that one can know such observables for the hydrogen atom—if one has the tools.

Example 12.3

Assume that the helium wavefunction is a product of two hydrogen-like wavefunctions (that is, neglect the term for the repulsion between the electrons) in the $n = 1$ principal quantum shell. Determine the electronic energy of the helium atom and compare it to the experimentally determined energy of -1.265×10^{-17} J. (Total energies are determined experimentally by measuring how much energy it takes to remove all of the electrons from an atom.)

Solution

Using equation 12.6 and neglecting the electron-repulsion term by assuming that the wavefunction is the product of two hydrogen-like wavefunctions:

$$\Psi_{\text{He}} = \Psi_{\text{H},1} \times \Psi_{\text{H},2}$$

the Schrödinger equation for the helium atom can be approximated as

$$\left[\left(-\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1}\right) + \left(-\frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2}\right)\right]\Psi_{\text{H},1}\Psi_{\text{H},2} \approx E_{\text{He}}\Psi_{\text{H},1}\Psi_{\text{H},2}$$

where E_{He} is the energy of the helium atom. Because the first term in brackets is a function of only electron 1 and the second term in the brackets is a function of only electron 2, this Schrödinger equation can be separated just like a two-dimensional particle-in-a-box can be separated. Understanding this, we can separate the Schrödinger equation above into two parts:

$$\left(-\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1}\right)\Psi_{\text{H},1} = E_1\Psi_{\text{H},1}$$

$$\left(-\frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2}\right)\Psi_{\text{H},2} = E_2\Psi_{\text{H},2}$$

where $E_{\text{He}} = E_1 + E_2$. These expressions are simply the one-electron Schrödinger equations for a hydrogen-like atom where the nuclear charge equals 2. An expression for the energy eigenvalue for such a system is known. From the previous chapter, it is

$$E = -\frac{Z^2e^4\mu}{8\epsilon_0^2h^2n^2}$$

for each hydrogen-like energy. For this approximation, we are assuming that helium is the sum of two hydrogen-like energies. Therefore,

$$\begin{aligned} E_{\text{He}} &= E_{\text{H},1} + E_{\text{H},2} \\ &= -\frac{2^2e^4\mu}{8\epsilon_0^2h^2n^2} - \frac{2^2e^4\mu}{8\epsilon_0^2h^2n^2} = -\frac{e^4\mu}{\epsilon_0^2h^2n^2} \end{aligned}$$

where we get the final term by combining the two terms to the left. Keep in mind that μ is the reduced mass for an electron about a helium nucleus, and that the principal quantum number is 1 for both terms. Substituting the values of the various constants, along with the value for the reduced mass of the electron-helium nucleus system (9.108×10^{-31} kg), we get

$$E_{\text{He}} = -1.743 \times 10^{-17}\ \text{J}$$

which is low by ~37.8% compared to experiment. Ignoring the repulsion between the electrons leads to a significant error in the total energy of the system, so a good model of the He atom should *not* ignore electron-electron repulsion.

The example above shows that assuming that the electrons in helium—and any other multielectron atom—are simple combinations of hydrogen-like electrons is naive assumption, and predicts quantized energies that are far from the experimentally measured values. We need other ways to better estimate the energies of such systems.

12.4 Spin Orbitals and the Pauli Principle

Example 12.3 for the helium atom assumed that both electrons have a principal quantum number of 1. If the hydrogen-like wavefunction analogy were taken further, we might say that both electrons are in the *s* subshell of the first shell—that they are in 1*s* orbitals. Indeed, there is experimental evidence (mostly spectra) for this assumption. What about the next element, Li? It has a third electron. Would this third electron also go into an approximate 1*s* hydrogen-like orbital? Experimental evidence (spectra) shows that it doesn't. Instead, it occupies what is approximately the *s* subshell of the second principal quantum shell: it is considered a 2*s* electron. Why doesn't it occupy the 1*s* shell?

We begin with the assumption that the electrons in a multielectron atom can in fact be assigned to *approximate* hydrogen-like orbitals, and that the wavefunction of the complete atom is the *product* of the wavefunctions of each occupied orbital. These orbitals can be labeled with the $n\ell$ quantum number labels: 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, and so on. Each *s*, *p*, *d*, *f*, . . . subshell can also be labeled by an m_ℓ quantum number, where m_ℓ ranges from $-\ell$ to ℓ ($2\ell + 1$ possible values). But it can also be labeled with a spin quantum number m_s, either $+\frac{1}{2}$ or $-\frac{1}{2}$. The spin part of the wavefunction is labeled with either α or β, depending on the value of m_s for each electron. Therefore, there are several simple possibilities for the approximate wavefunction for, say, the lowest-energy state (the ground state) of the helium atom:

$$\Psi_{\text{He}} = (1s_1\alpha)(1s_2\alpha)$$

$$\Psi_{\text{He}} = (1s_1\alpha)(1s_2\beta)$$

$$\Psi_{\text{He}} = (1s_1\beta)(1s_2\alpha)$$

$$\Psi_{\text{He}} = (1s_1\beta)(1s_2\beta)$$

where the subscript on 1*s* refers to the individual electron. We will assume that each individual Ψ_{He} is normalized. Because each Ψ_{He} is a combination of a spin wavefunction and an orbital wavefunction, Ψ_{He}'s are more properly called *spin orbitals.*

Because spin is a vector and because vectors can add and subtract from each other, one can easily determine a *total spin* for each possible helium spin orbital. (It is actually a total *z component* of the spin.) For the first spin orbital equation above, both spins are α, so the total spin is $(+\frac{1}{2}) + (+\frac{1}{2}) = 1$. Similarly, for the last spin orbital, the total spin is $(-\frac{1}{2}) + (-\frac{1}{2}) = -1$. For the middle two spin orbitals, the total (*z*-component) spin is exactly zero. To summarize:

Approximate wavefunction	Total *z*-component spin
$\Psi_{He} = (1s_1\alpha)(1s_2\alpha)$	+1
$\Psi_{He} = (1s_1\alpha)(1s_2\beta)$	0
$\Psi_{He} = (1s_1\beta)(1s_2\alpha)$	0
$\Psi_{He} = (1s_1\beta)(1s_2\beta)$	−1

At this point, experimental evidence can be introduced. (The necessity of comparing the predictions of theory with experiment should not be forgotten.) Angular momenta of charged particles can be differentiated by magnetic fields, so there is a way to experimentally determine whether or not atoms have an overall angular momentum. Since spin is a form of angular momentum, it should not be surprising that magnetic fields can be used to determine the overall spin in an atom. Experiments show that ground-state helium atoms have zero *z*-component spin. This means that of the four approximate wavefunctions listed above, the first and last are not acceptable because they do not agree with experimentally determined facts. Only the middle two, $(1s_1\alpha)(1s_2\beta)$ and $(1s_1\beta)(1s_2\alpha)$, can be considered for helium.

Which wavefunction of the two is acceptable, or are they both? One can suggest that both wavefunctions are acceptable and that the helium atom is doubly degenerate. This turns out to be an unacceptable statement because, in part, it implies that an experimenter can determine without doubt that electron 1 has a certain spin wavefunction and that electron 2 has the other spin wavefunction. Unfortunately, we cannot tell one electron from another. They are indistinguishable.

This indistinguishability suggests that the best way to describe the electronic wavefunction of helium is not by each wavefunction individually, but by a combination of the possible wavefunctions. Such combinations are usually considered as sums and/or differences. Given *n* wavefunctions, one can mathematically determine *n* different combinations that are linearly independent. So, for the two "acceptable" wavefunctions of He, two possible combinations can be constructed to account for the fact that electrons are indistinguishable. These two combinations are the sum and the difference of the two individual spin orbitals:

$$\Psi_{He,1} = \frac{1}{\sqrt{2}}[(1s_1\alpha)(1s_2\beta) + (1s_1\beta)(1s_2\alpha)]$$

$$\Psi_{He,2} = \frac{1}{\sqrt{2}}[(1s_1\alpha)(1s_2\beta) - (1s_1\beta)(1s_2\alpha)]$$

The term $1/\sqrt{2}$ is a renormalization factor, taking into account the combination of two normalized wavefunctions. These combinations have the proper form for possible wavefunctions of the helium atom.

Are both acceptable, or only one of the two? At this point we rely on a postulate proposed by Wolfgang Pauli in 1925, which was based on the study of atomic spectra and the increasing understanding of the necessity of quantum numbers. Since electrons are indistinguishable, one particular electron in helium can be either electron 1 or 2. We can't say for certain which. But because the electron has a spin of $\frac{1}{2}$, it has certain properties that affect its wavefunction (the details of which cannot be considered here). If electron 1 were *exchanged* with electron 2, Pauli postulated, the complete wavefunction *must change sign.* Mathematically, this is written as

$$\Psi(1, 2) = -\Psi(2, 1)$$

The switch in order of writing the labels 1 and 2 implies that the two electrons are exchanged. Electron 1 now has the coordinates of electron 2, and vice versa. A wavefunction having this property is called *antisymmetric.* (By contrast, if $\Psi(1, 2) = \Psi(2, 1)$, the wavefunction is labeled *symmetric.*) Particles having half-integer spin ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$) are collectively called *fermions.* The *Pauli principle* states that fermions must have antisymmetric wavefunctions with respect to exchange of particles. Particles having integer spins, called *bosons,* are restricted to having symmetric wavefunctions with respect to exchange.

Electrons are fermions (having spin $= \frac{1}{2}$) and so according to the Pauli principle must have antisymmetric wavefunctions. Consider, then, the two possible approximate wavefunctions for helium. They are

$$\Psi_{\text{He},1} = \frac{1}{\sqrt{2}}[(1s_1\alpha)(1s_2\beta) + (1s_1\beta)(1s_2\alpha)] \tag{12.7}$$

$$\Psi_{\text{He},2} = \frac{1}{\sqrt{2}}[(1s_1\alpha)(1s_2\beta) - (1s_1\beta)(1s_2\alpha)] \tag{12.8}$$

Are either of these antisymmetric? We can check by interchanging electrons 1 and 2 in the first wavefunction, equation 12.7, and get

$$\Psi(2, 1) = \frac{1}{\sqrt{2}}[(1s_2\alpha)(1s_1\beta) + (1s_2\beta)(1s_1\alpha)]$$

(Note the change in the subscripts 1 and 2.) This should be recognized as the original wavefunction $\Psi(1, 2)$, only algebraically rearranged. (Show this.) However, upon electron exchange, the second wavefunction, equation 12.8, becomes

$$\Psi(2, 1) = \frac{1}{\sqrt{2}}[(1s_2\alpha)(1s_1\beta) - (1s_2\beta)(1s_1\alpha)] \tag{12.9}$$

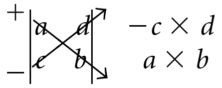
which can be shown algebraically to be $-\Psi(1, 2)$. (Show this, also.) Therefore, this wavefunction is antisymmetric with respect to exchange of electrons and, by the Pauli principle, is a proper wavefunction for the spin orbitals of the helium atom. Equation 12.8, but not equation 12.7, represents the correct form for a spin-orbital wavefunction of the ground state of He.

The rigorous statement of the Pauli principle is that wavefunctions of electrons must be antisymmetric with respect to exchange of electrons. There is a simpler statement of the Pauli principle. It comes from the recognition that equation 12.8, the only acceptable wavefunction for helium, can be written in terms of a matrix determinant.

Recall that the determinant of a 2 × 2 matrix written as

$$\begin{vmatrix} a & d \\ c & b \end{vmatrix}$$

is simply $(a \times b) - (c \times d)$, which is remembered mnemonically as



The proper antisymmetric wavefunction, equation 12.8, for the helium atom can also be written in terms of a 2 × 2 determinant:

$$\Psi_{\text{He}} = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s_1\alpha & 1s_1\beta \\ 1s_2\alpha & 1s_2\beta \end{vmatrix} \tag{12.10}$$

The term $1/\sqrt{2}$ multiplies the entire determinant, like it multiplies the entire wavefunction in equation 12.8. Such determinants used to represent an antisymmetric wavefunction are called *Slater determinants,* after J. C. Slater, who pointed out such constructions for wavefunctions in 1929.

The use of Slater determinants to express wavefunctions that are automatically antisymmetric stems from the fact that when two rows (or two columns) of a determinant are exchanged, the determinant of the matrix becomes negated. In the Slater determinant shown in equation 12.10, the possible spin orbitals for electron 1 are listed in the first row and the spin orbitals of electron 2 are listed in the second row. Switching these two rows would be the same thing as exchanging the two electrons in the helium atom. When this happens, the determinant changes sign, which is what the Pauli principle requires for acceptable wavefunctions of fermions. Writing a wavefunction in terms of a proper Slater determinant guarantees an antisymmetric wavefunction.

The Slater-determinant form of a wavefunction guarantees something else, which leads to the simplified version of the Pauli principle. Suppose both electrons in helium had the exact same spin orbital. The determinant part of the wavefunction would have the form

$$\begin{vmatrix} 1s_1\alpha & 1s_1\alpha \\ 1s_2\alpha & 1s_2\alpha \end{vmatrix} \quad \text{which is exactly 0} \tag{12.11}$$

The determinant being exactly zero is a general property of determinants. (If any two columns or rows of a determinant are the same, the value of the determinant is zero.) Therefore the wavefunction is identically zero and this state will not exist. The same conclusion can be reached if the spin on both electrons is β. Consider, then, the lithium atom. Assuming that all three electrons were in the 1*s* shell, the only two possible determinant forms of the wavefunction would be (depending on the spin function on the third electron):

$$\begin{vmatrix} 1s_1\alpha & 1s_1\beta & 1s_1\alpha \\ 1s_2\alpha & 1s_2\beta & 1s_2\alpha \\ 1s_3\alpha & 1s_3\beta & 1s_3\alpha \end{vmatrix} \quad \text{or} \quad \begin{vmatrix} 1s_1\alpha & 1s_1\beta & 1s_1\beta \\ 1s_2\alpha & 1s_2\beta & 1s_2\beta \\ 1s_3\alpha & 1s_3\beta & 1s_3\beta \end{vmatrix} \tag{12.12}$$

Note that in both cases, two columns of the determinant represent the same spin orbitals for two of the three electrons (1st and 3rd columns for the first determinant, 2nd and 3rd columns for the second determinant). The mathematics of determinants requires that if any two rows or columns are exactly the same, the value of the determinant is exactly zero. One cannot have a wavefunction for Li having three electrons in the 1*s* shell. The third electron, instead, *must* be in a different shell. The next shell and subshell are 2*s*.

As we have been assigning a set of four quantum numbers to electrons in hydrogen-like orbitals, we can do so for the spin orbitals of multielectron atoms where we are approximating hydrogen-like orbitals. In the first row of equation 12.11, the two spin orbitals can be represented by the set of four quantum numbers (n, ℓ, m_ℓ, m_s) as being $(1, 0, 0, \frac{1}{2})$ and $(1, 0, 0, \frac{1}{2})$: the same four quantum numbers. (Can you see how these numbers were determined from the expression for the spin orbital?) In the first row of equation 12.12, the three spin orbitals in the first case have the sets $(1, 0, 0, \frac{1}{2})$, $(1, 0, 0, -\frac{1}{2})$, and $(1, 0, 0, \frac{1}{2})$: the first and third spin orbitals are the same. In the second case, for the first row, the spin orbitals can be represented by the quantum numbers $(1, 0, 0, \frac{1}{2})$, $(1, 0, 0, -\frac{1}{2})$, and $(1, 0, 0, -\frac{1}{2})$, with the second and third spin orbitals having the same set of four quantum numbers. In all three cases, other rows of the Slater determinant can have quantum numbers assigned to them, and in all cases the determinant is exactly zero, implying that the overall wavefunction does not exist.

On this basis, one consequence of the Pauli principle is that *no two electrons in any system can have the same set of four quantum numbers.* (This statement is sometimes used in place of the original statement of the Pauli principle.) This means that each and every electron must have its own unique spin orbital, and since there are only two possible spin functions for an electron, each orbital can be assigned only two electrons. Therefore, an *s* subshell can accommodate two electrons maximum; each *p* subshell, with three individual *p* orbitals, can hold a maximum of six electrons; each *d* subshell, with five *d* orbitals, can hold ten electrons; and so on. Because this consequence of the Pauli principle excludes spin orbitals from having more than one electron, Pauli's statement is commonly referred to as the *Pauli exclusion principle.*

Example 12.4

Show for each row of the Slater determinants for Li in equation 12.12 that the wavefunction represented by the determinant violates the Pauli exclusion principle.

Solution

By row, the set of four quantum numbers for each spin orbital is listed:

$$\begin{vmatrix} 1s_1\alpha & 1s_1\beta & 1s_1\alpha \\ 1s_2\alpha & 1s_2\beta & 1s_2\alpha \\ 1s_3\alpha & 1s_3\beta & 1s_3\alpha \end{vmatrix} \quad \begin{matrix} (1, 0, 0, \tfrac{1}{2}) & (1, 0, 0, -\tfrac{1}{2}) & (1, 0, 0, \tfrac{1}{2}) \\ (1, 0, 0, \tfrac{1}{2}) & (1, 0, 0, -\tfrac{1}{2}) & (1, 0, 0, \tfrac{1}{2}) \\ (1, 0, 0, \tfrac{1}{2}) & (1, 0, 0, -\tfrac{1}{2}) & (1, 0, 0, \tfrac{1}{2}) \end{matrix}$$

$$\begin{vmatrix} 1s_1\alpha & 1s_1\beta & 1s_1\beta \\ 1s_2\alpha & 1s_2\beta & 1s_2\beta \\ 1s_3\alpha & 1s_3\beta & 1s_3\beta \end{vmatrix} \quad \begin{matrix} (1, 0, 0, \tfrac{1}{2}) & (1, 0, 0, -\tfrac{1}{2}) & (1, 0, 0, -\tfrac{1}{2}) \\ (1, 0, 0, \tfrac{1}{2}) & (1, 0, 0, -\tfrac{1}{2}) & (1, 0, 0, -\tfrac{1}{2}) \\ (1, 0, 0, \tfrac{1}{2}) & (1, 0, 0, -\tfrac{1}{2}) & (1, 0, 0, -\tfrac{1}{2}) \end{matrix}$$

In each case, two of the three entries in each row have the same set of four quantum numbers and so the wavefunction is not allowed by the Pauli exclusion principle.

Wavefunctions written in terms of a Slater determinant have a normalization factor of $1/\sqrt{n!}$, where n is the number of rows or columns in the determinant (and equals the number of electrons in the atom). This is because the expanded form of the wavefunction Ψ has $n!$ terms. In constructing Slater determinants, we will follow the custom of writing the individual spin orbitals going across, two spatial wavefunctions with an α and a β spin wavefunction each, and listing the electrons sequentially going down. That is:

$$\begin{array}{r|ccccc|} & \multicolumn{5}{c}{\xrightarrow{\text{spin orbitals}}} \\ \text{electron 1} & 1s\alpha & 1s\beta & 2s\alpha & 2s\beta & \ldots \\ \text{electron 2} & 1s\alpha & 1s\beta & 2s\alpha & 2s\beta & \ldots \\ \text{electron 3} & \ldots & \ldots & \ldots & \ldots & \ldots \\ \vdots & \multicolumn{5}{c}{} \end{array}$$

Going across the determinant, the spin part alternates: $\alpha, \beta, \alpha, \beta, \ldots$. You also have to keep track of the n, ℓ, and m_ℓ quantum numbers to make sure each shell and subshell is represented in the proper order and number. The following example illustrates the use of this idea.

Example 12.5

The third electron in Li goes into the 2*s* orbital. Assuming a (re)normalization constant of $1/\sqrt{6}$, construct a proper antisymmetric wavefunction for Li in terms of a Slater determinant.

Solution

The rows will represent electrons 1, 2, and 3; the columns will represent the spin orbitals $1s\alpha$, $1s\beta$, and $2s\alpha$ (or $2s\beta$). Following the determinant setup above, the antisymmetric wavefunction is

$$\Psi_{\mathrm{Li}} = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s_1\alpha & 1s_1\beta & 2s_1\alpha \\ 1s_2\alpha & 1s_2\beta & 2s_2\alpha \\ 1s_3\alpha & 1s_3\beta & 2s_3\alpha \end{vmatrix}$$

Because there are two possible wavefunctions for Li (depending on whether the spin orbital for the last column is $2s\alpha$ or $2s\beta$), we conclude that this energy level is doubly degenerate.

12.5 Other Atoms and the Aufbau Principle

We have presumed, more than proved, that multielectron atoms can be conceptually approximated as combinations of hydrogen-like orbitals (even though our helium example showed that the predicted energies are not very close). Further, the Pauli principle restricts orbitals to having only two electrons, each with different spin. As we consider larger and larger atoms, electrons in these atoms will occupy orbitals described with larger and larger principal quantum numbers.

Recall that in the hydrogen atom, the principal quantum number is the only quantum number that affects the total energy. This is not the case with multielectron atoms, because interelectronic interactions affect the energies of the orbitals, and now the subshells within the shells have different energies. Figure 12.4 illustrates what happens to the electronic energy levels of atoms. In the case of hydrogen, energies of orbitals are determined by a single quantum number. In multielectron atoms, the principal quantum number is an important factor in the energy of an orbital, but the angular momentum quantum number is also a factor. (To a much lesser extent, the m_ℓ and m_s quantum numbers also affect the exact energy of a spin orbital, but their effect on the energy is more noticeable in molecules. Their effect on the exact energies of electrons is practically negligible for atoms outside of magnetic fields. See Figure 12.2 for an example.)

When assigning electrons to orbitals in multielectron atoms, it might be assumed that they will occupy the available shell and subshell having the lowest energy. This is a misstatement. Electrons reside in the next available spin orbital that yields the *lowest total energy for the atom*. The placement is not necessarily determined by the individual energy of the spin orbital. Instead, the total energy of the atom must be considered. When an atom's electrons occupy orbitals that yield the lowest total energy, the atom is said to be in its *ground state*. Any other electronic state, which by definition would have a higher total energy, is considered an *excited state*. The electrons in an atom can reach excited states by absorbing energy; this is one of the basic processes in spectroscopy.

Consider an atom of the element beryllium, which has four electrons. Two of the electrons occupy the orbital labeled 1*s*. The two remaining electrons occupy an orbital in the second shell, but which? The $n = 2$ shell has $\ell = 0$

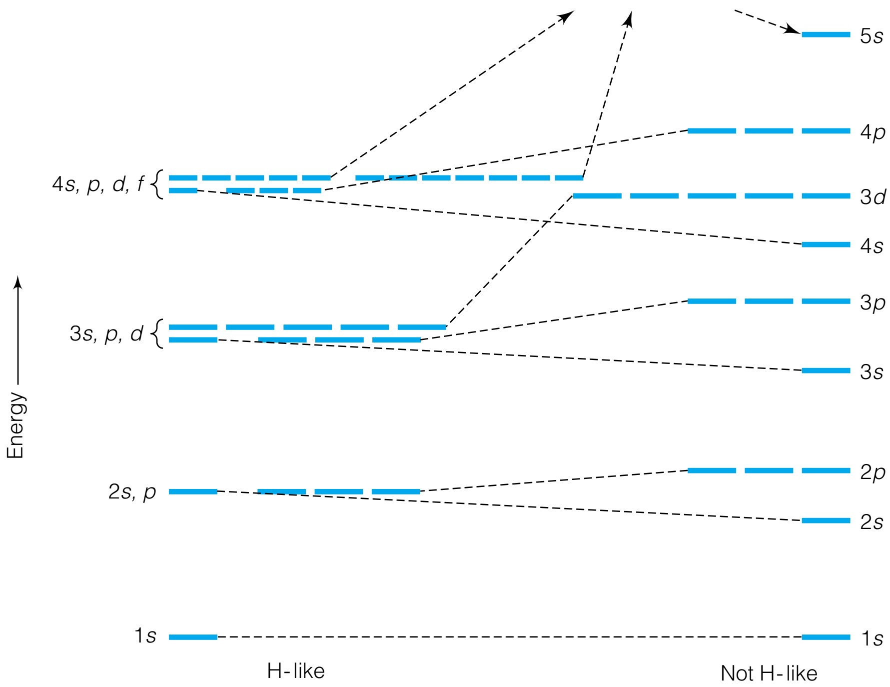


Figure 12.4 The effect of more than one electron on the electronic energy levels of an atom. For hydrogen-like atoms, all of the energy levels with the same principal quantum number n are degenerate. For atoms having more than one electron, the shells are separated by the ℓ quantum number as well. (Energy axis is not to scale.)

and $\ell = 1$, so that the possible subshells are 2*s* and 2*p*. Because of the slightly higher energy of the 2*p* subshell, the electrons occupy the 2*s* subshell, which can hold two electrons if they have different spin functions. The occupation of orbitals in an atom is listed as an *electron configuration,* using superscripts to indicate the number of electrons in each individual subshell. It is assumed that for ground states, the spins of the electrons are appropriate and satisfy the Pauli exclusion principle. The electron configuration for Be is written as

$$1s^2\ 2s^2$$

This is an obvious electron configuration, since the 2*p* subshell is higher in energy than the 2*s*, as shown in Figure 12.4. However, as we will see shortly, it is not always so straightforward to assign an electron configuration.

Example 12.6

Electron configurations are rather abbreviated when compared to the more complete Slater-determinant form of the antisymmetric wavefunction. Compare the electron configuration of Be with the Slater-determinant form of Ψ for Be.

Solution

The electron configuration for Be, given above, is simply $1s^2\ 2s^2$. Using the rule from above for constructing Slater determinants, the more complete Ψ is

$$\Psi = \frac{1}{\sqrt{24}}\begin{vmatrix} 1s_1\alpha & 1s_1\beta & 2s_1\alpha & 2s_1\beta \\ 1s_2\alpha & 1s_2\beta & 2s_2\alpha & 2s_2\beta \\ 1s_3\alpha & 1s_3\beta & 2s_3\alpha & 2s_3\beta \\ 1s_4\alpha & 1s_4\beta & 2s_4\alpha & 2s_4\beta \end{vmatrix}$$

Written as a determinant, this wavefunction is indeed antisymmetric. If the determinant were evaluated, it would expand into 24 terms. The electron configuration, however, is a total of only six alphanumeric characters. Although the Slater-determinant wavefunction is more complete, the electron configuration is much more convenient.

As we consider larger and larger atoms, electrons start occupying orbitals of the $2p$ subshell. It should be recognized that with three possible p orbitals, there are several possible ways of, say, two electrons occupying the various p orbitals. A statement known as *Hund's rule* indicates that electrons occupy each degenerate orbital singly before pairing up orbitals with two electrons of opposite spin. (The rule was enunciated by Friedrich Hund in 1925 after detailed consideration of atomic spectra.) In the absence of any other influence, the orbitals are still degenerate, so at this point there is no preference about which p orbitals are singly, then doubly, occupied. Therefore, one specific electron configuration for the ground state of boron can be listed as $1s^2\ 2s^2\ 2p_x^1$, and a specific electron configuration for the ground state of carbon can be given as $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$. If Hund's rule is assumed, a more general electron configuration of C can be abbreviated as $1s^2\ 2s^2\ 2p^2$.

Example 12.7

List two other acceptable ground-state electron configurations for B and C. Give an unacceptable ground-state electron configuration for C.

Solution

Since it does not matter which p orbitals are used, the ground state of B can also be written as $1s^2\ 2s^2\ 2p_y^1$ or $1s^2\ 2s^2\ 2p_z^1$. For C, the other acceptable electron configurations are $1s^2\ 2s^2\ 2p_y^1\ 2p_z^1$ or $1s^2\ 2s^2\ 2p_x^1\ 2p_z^1$. Both of these can be abbreviated as $1s^2\ 2s^2\ 2p^2$. An unacceptable ground-state electron configuration might be $1s^2\ 2s^2\ 2p_x^2$, since this has the electrons paired in a single p orbital rather than spread out among the degenerate p orbitals, as required by Hund's rule.

The filling of the spin orbitals so far has taken the order $1s$, $2s$, $2p$. As one considers the electron configurations of larger atoms, electrons continue to occupy orbitals through $3s$ and $3p$. But at potassium ($Z = 19$), instead of filling the $3d$ orbital, the $4s$ orbital is occupied first. Only after a second electron occupies the $4s$ orbital (for calcium) does the $3d$ subshell start becoming occupied with electrons.

Why? The naive answer is that the $4s$ orbital is lower in energy than the $3d$ orbital. Since the energies of orbitals in multielectron atoms are determined by the quantum number ℓ as well as the quantum number n, it must be at this point that the energy E_{4s} becomes less than the energy E_{3d}. Actually, this argument is misleading. The reason that the $4s$ orbital becomes occupied is that the *total* energy of the atom is less than it would be if the electron occupied a $3d$ orbital.

On the face of it, this seems peculiar. If the $3d$ orbital were lower in energy, why shouldn't it be occupied by an electron first? If it were a hydrogen-like atom, with only a single electron, then the absolute energy of the orbital would

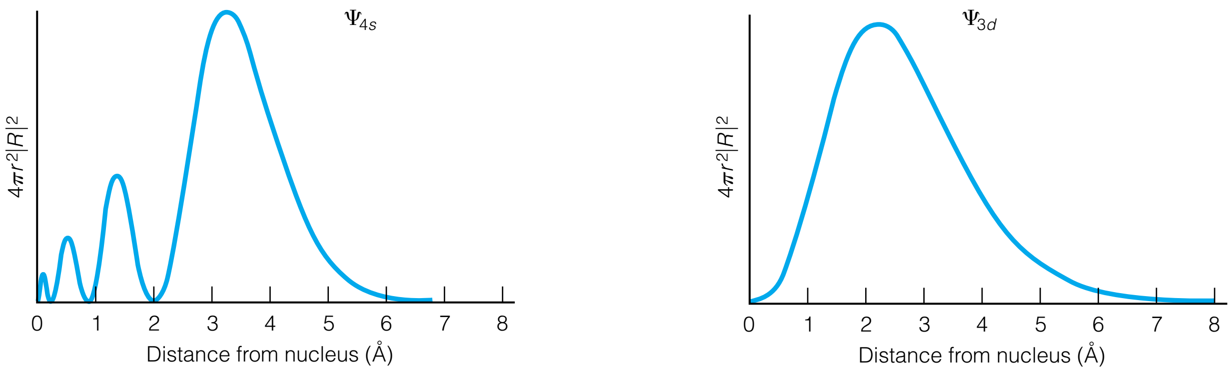


Figure 12.5 Plots of $4\pi r^2|R|^2$ for the $3d$ and $4s$ wavefunctions. Note that the plots have the same x-axis, and that the $4s$ electron has some probability of being rather close to the nucleus. For multielectron atoms, the penetration of the $4s$ electron combined with the shielding effect of the other electrons serves to make the $4s$ orbital the next one occupied by electrons, rather than the $3d$.

be the only factor determining the order of orbital occupation. But in multielectron atoms, there is an additional factor. Not only is the absolute energy of the orbital a factor, but the amount an electron in that orbital *interacts with the other electrons and the nucleus* is also a criterion in determining the total energy of an atom.

To illustrate this point, Figure 12.5 shows the probabilities of the radial functions in spherically symmetric shells about the nucleus (that is, $4\pi r^2|R|^2$ versus r) for the $3d$ and $4s$ hydrogen-like wavefunctions on the same scale. Both wavefunctions show a maxima several angstroms from the nucleus.* However, note that the $4s$ orbital has three relative maxima before its absolute maximum, and that several of these maxima indicate that an electron in a $4s$ orbital has a considerable probability of being closer to the nucleus than an electron in a $3d$ orbital. An electron in a $4s$ orbital is said to *penetrate* inward toward the nucleus. The increased penetration of the negatively charged $4s$ electron toward the positively charged nucleus means an additional energy stabilization of the system as a whole, and as a result the final electron in K occupies the $4s$ orbital. This allows the entire K atom to have a lower total energy. And even though some energy of repulsion erases some of that energy gain, the last electron of Ca, the next largest atom, also occupies a $4s$ orbital instead of a $3d$ orbital, pairing up with the first electron in the $4s$ orbital. (However, there are a few exceptions, as a review of electron configurations will show.) Only with the introduction of another electron, for an atom of scandium, does the electron occupy a $3d$ orbital instead of a $4p$ orbital.

This building up of electron configurations by placing electrons in orbitals is called the *aufbau principle* (the name of the principle comes from the German word *aufbauen,* meaning “to build up”). Although it might seem at this point that there is little regularity in building up electron configurations of larger atoms, there is some level of consistency. For example, the periodic table’s shape is dictated by the filling of the orbitals by electrons. The number of valence electrons almost never exceeds 8, due to the eventual regularity in the filling of orbitals. There are several mnemonic devices used to remember

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*Actually, in a multielectron atom the maxima would be somewhat farther out because of a shielding effect on the nucleus by the electrons occupying the inner shells.

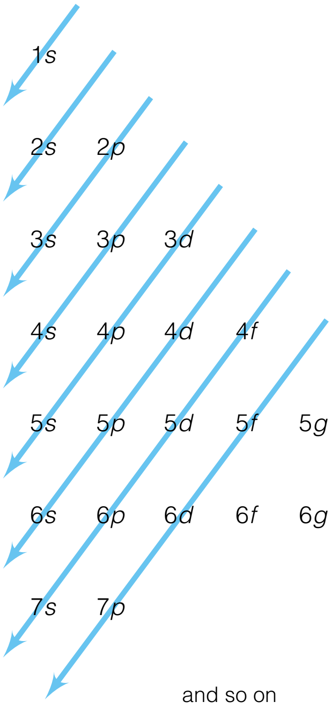

Figure 12.6 A convenient way to remember the order of filling of the subshells in most atoms (1–85). Simply follow the order of subshells crossed by the arrows.

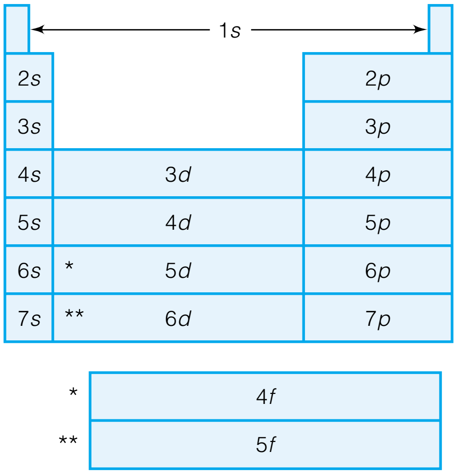

Figure 12.7 The aufbau principle rationalizes the structure of the periodic table. Compare the order of filling of the subshells in Figure 12.6 with the labels in the periodic table here. (Note where the 4*f* and 5*f* subshells are filled.)

the order in which orbitals are filled by electrons. Perhaps the most common is shown in Figure 12.6. This ordering of orbitals, and the idea that each subshell is completely filled before electrons occupy the next orbital, is strictly applicable to the electron configurations of 85 of the first 103 elements. (There is little or no experimental verification of the electron configurations of elements 104 or larger to date.) Figure 12.7 shows the relationship between the aufbau principle and the structure of the periodic table. Table 12.1 lists the electron configurations of the elements in their lowest electronic states.

12.6 Perturbation Theory

In a previous section, we presumed that the wavefunctions of multielectron atoms can be approximated as products of hydrogen-like orbitals:

$$\Psi_Z \cong \Psi_{\mathrm{H},1} \cdot \Psi_{\mathrm{H},2} \cdot \Psi_{\mathrm{H},3} \cdots \Psi_{\mathrm{H},Z} \tag{12.13}$$

where Ψ_Z is the wavefunction for an atom having a nuclear charge of Z and $\Psi_{\mathrm{H},1}, \ldots . \Psi_{\mathrm{H},Z}$ are the hydrogen-like wavefunctions for each of the Z electrons. Generally speaking, this is a very useful *qualitative* description of the electrons in larger atoms. However, we did see that in the case of He, it is not a good system for making a *quantitative* prediction of the total electronic energy of the system. As noted, there is no known exact solution to the differential equation that is the Schrödinger equation for the helium atom; it has no *analytic* solution. There is no known simple (or complicated, for that matter!) expression for Ψ that we can substitute into the Schrödinger equation as given in equation 12.5 and have it satisfied so that an eigenvalue E is produced.

Table 12.1 Ground-state electron configurations of the elements[a]

H	$1s^1$
He	$1s^2$
Li	$1s^2 2s^1$
Be	$1s^2 2s^2$
B	$1s^2 2s^2 2p^1$
C	$1s^2 2s^2 2p^2$
N	$1s^2 2s^2 2p^3$
O	$1s^2 2s^2 2p^4$
F	$1s^2 2s^2 2p^5$
Ne	$1s^2 2s^2 2p^6$
Na	$1s^2 2s^2 2p^6 3s^1$
Mg	$1s^2 2s^2 2p^6 3s^2$
Al	$1s^2 2s^2 2p^6 3s^2 3p^1$
Si	$1s^2 2s^2 2p^6 3s^2 3p^2$
P	$1s^2 2s^2 2p^6 3s^2 3p^3$
S	$1s^2 2s^2 2p^6 3s^2 3p^4$
Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$
Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$
K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
V	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
Cr*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
Co	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$
Cu*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
Zn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$
Ga	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$
Ge	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$
As	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$
Se	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$
Br	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$
Kr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$
Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$
Sr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2$
Y	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^1$
Zr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$
Nb*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1 4d^4$
Mo*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1 4d^5$
Tc	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^5$
Ru*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1 4d^7$
Rh*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1 4d^8$
Pd*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^0 4d^{10}$
Ag*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1 4d^{10}$
Cd	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10}$
In	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^1$
Sn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^2$
Sb	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^3$
Te	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^4$
I	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^5$
Xe	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$
Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1$
Ba	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2$
La*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 5d^1$
Ce*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^1 5d^1$
Pr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^3$
Nd	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^4$
Pm	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^5$
Sm	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$
Eu	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^7$
Gd*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^7 5d^1$
Tb	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^9$
Dy	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{10}$
Ho	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{11}$
Er	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{12}$
Tm	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{13}$
Yb	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14}$
Lu	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^1$
Hf	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^2$
Ta	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^3$
W	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^4$
Re	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^5$
Os	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^6$
Ir	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^7$
Pt*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1 4f^{14} 5d^9$
Au*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1 4f^{14} 5d^{10}$
Hg	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10}$
Tl	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^1$
Pb	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^2$
Bi	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^3$
Po	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^4$
At	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^5$
Rn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6$
Fr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^1$
Ra	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2$
Ac*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 6d^1$
Th*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 6d^2$
Pa*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^2 6d^1$
U*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^3 6d^1$
Np*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^4 6d^1$
Pu	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^6$
Am	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^7$
Cm*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^7 6d^1$
Bk	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^9$
Cf	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{10}$
Es	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{11}$
Fm	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{12}$
Md	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{13}$
No	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14}$
Lr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 6d^1$

[a] An asterisk by the symbol indicates that the electron configuration does not exactly conform to the strict rules of the aufbau principle. However, in almost all cases, the variance is due to a single electron. Only elements up to $Z = 103$ are included, since the electron configurations for elements beyond that have not been experimentally verified.

That does not mean that there is no understanding of, or recourse for, such systems. Nor does it imply that quantum mechanics is a useless theory for these systems. There are two main tools for applying quantum mechanics to systems whose Schrödinger equations cannot be solved exactly. Use of either depends on the type of system under study as well as what information you want to determine.

The first of these tools is called *perturbation theory.* Perturbation theory assumes that a system can be approximated as a known, solvable system and that any difference between the system of interest and the known system is a small, additive perturbation that can be calculated separately and added on. We will assume that all of the energy levels under discussion are singly degenerate, so this tool is more appropriately named *nondegenerate perturbation theory.* Also, perturbation theory can be taken to very complex levels. Here, we focus on the first level of approximation, which is called *first-order* perturbation theory.

Perturbation theory assumes that the Hamiltonian for a real system can be written as

$$\hat{H}_{\text{system}} = \hat{H}_{\text{ideal}} + \hat{H}_{\text{perturb}} \equiv \hat{H}^{\circ} + \hat{H}' \tag{12.14}$$

where $\hat{H}_{\text{system}}$ is the Hamiltonian of the system of interest that is being approximated, $\hat{H}^{\circ}$ is the Hamiltonian of an ideal or model system, and $\hat{H}'$ represents the small, additive perturbation. For example, in the case of the helium atom, the ideal part of the Hamiltonian can represent two hydrogen-like atoms. The perturbation part of the Hamiltonian can represent the coulombic repulsion between the electrons:

$$\hat{H}_{\text{He}} = (\hat{H}_{\text{H-like}} + \hat{H}_{\text{H-like}}) + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

(In this case, there are two hydrogen-like Hamiltonians because there are two electrons. Despite this rewriting, the Schrödinger equation for He has not really changed and is still analytically unsolvable.) Any number of additive perturbations can be combined with an ideal Hamiltonian. It is, of course, easier to keep the number of terms in the Hamiltonian as small as possible. What is usually found is that there is a trade-off between the number of terms and the accuracy of the solution to the Schrödinger equation.

If we assume that the wavefunction Ψ of the real system is similar to the wavefunction of the ideal system, denoted $\Psi^{(0)}$, then one can say that, *approximately,*

$$\hat{H}_{\text{system}}\Psi^{(0)} \approx E_{\text{system}}\Psi^{(0)} \tag{12.15}$$

where E_{system} is the eigenvalue for the energy of the real system. Over the course of many observations, one eventually determines an average value of the observable energy, $\langle E \rangle$. By using one of the postulates of quantum mechanics $\langle E \rangle$ can be approximated by the expression

$$\langle E \rangle \approx \int (\Psi^{(0)})^* \hat{H}_{\text{system}} \Psi^{(0)}\, d\tau \tag{12.16}$$

Given the form of $\hat{H}_{\text{system}}$, one can substitute into equation 12.16 and partially evaluate:

$$\begin{aligned} \langle E \rangle &\approx \int (\Psi^{(0)})^* (\hat{H}^{\circ} + \hat{H}')\Psi^{(0)}\, d\tau \\ &= \int (\Psi^{(0)})^* \hat{H}^{\circ} \Psi^{(0)}\, d\tau + \int (\Psi^{(0)})^* \hat{H}' \Psi^{(0)}\, d\tau \\ &= \langle E^{(0)} \rangle + \int (\Psi^{(0)})^* \hat{H}' \Psi^{0}\, d\tau = \langle E^{(0)} \rangle + \langle E^{(1)} \rangle \end{aligned} \tag{12.17}$$

where $\langle E^{(0)} \rangle$ is the average energy of the ideal or model system (that is, an eigenvalue energy, usually) and $\langle E^{(1)} \rangle$ is the *first-order correction* to the energy. Thus, the first approximation to the energy of a real system is equal to the ideal energy plus some additional amount given by $\int (\Psi^{(0)})^* \widehat{H}' \Psi^{(0)}\, d\tau$. If this integral can be evaluated or approximated, then a correction to the energy can be determined. What equation 12.17 means is that when we write a Hamiltonian as a perturbed ideal operator, the energy—the observable associated with the Hamiltonian—is also perturbed from the ideal.

Example 12.8

What is the correction to the energy of the helium atom, assuming that the perturbation can be approximated as a coulombic repulsion of the two electrons?

Solution

According to equation 12.17, the perturbation is

$$\langle E^{(1)} \rangle = \int (\Psi^{(0)})^* \frac{e^2}{4\pi\epsilon_0 r_{12}} \Psi^{(0)}\, d\tau$$

If some way can be found to evaluate this integral, a correction to the total energy—and thus a perturbation-theory approximation to the energy of a He atom—can be approximated.

The integral in the above example can be approximated by mathematical techniques and substitutions that we will not go into. (A discussion of its solution can be found in more advanced texts.) Approximations and substitutions are possible and the above integral can be estimated as

$$\langle E^{(1)} \rangle = \frac{5}{4}\left(\frac{e^2}{4\pi\epsilon_0 a_0}\right)$$

where e is the charge on the electron, ϵ_0 is the permittivity of free space, and a_0 is the first Bohr radius (0.529 Å). When we substitute the values of the constants into this expression, we get

$$\langle E^{(1)} \rangle = 5.450 \times 10^{-18}\ \text{J}$$

Combining this result with the "ideal" energy, which was determined by assuming the sum of two hydrogen electron energies (see Example 12.3), we get for the total energy of helium

$$E_{\text{He}} = -1.743 \times 10^{-17}\ \text{J} + 5.450 \times 10^{-18}\ \text{J} = -1.198 \times 10^{-17}\ \text{J}$$

which, when compared to the experimentally determined energy of the helium atom (given in Example 12.3 as -1.265×10^{-17} J), is found to be off by only 5.3%. Compared to the hydrogen-like approximation of helium, this is a big improvement. It points out the usefulness of perturbation theory.

Example 12.9

In a particle-in-a-box having length a, instead of being zero the potential energy in the box is a linear function of the position. That is,

$$V = kx$$

a. Using perturbation theory, estimate the average energy of a particle having mass m and whose motion is described by the lowest-energy wavefunction ($n = 1$).
b. The integral in part a can be solved exactly. Explain why this calculated value is not the exact value for the energy of a particle in this system.

Solution

a. According to perturbation theory, the energy of the particle is

$$\langle E\rangle = \langle E^{(0)}\rangle + \langle E^{(1)}\rangle$$

If one assumes that $\widehat{H}^\circ$ is the Hamiltonian for the particle-in-a-box, then the perturbation part $\widehat{H}'$ of the complete Hamiltonian is kx. According to equation 12.17, the energy is

$$\langle E\rangle = \frac{n^2h^2}{8ma^2} + \langle E^{(1)}\rangle$$

To evaluate $\langle E^{(1)}\rangle$, we must evaluate the integral

$$\langle E^{(1)}\rangle = \frac{2}{a}\int_0^a \left(\sin\frac{\pi x}{a}\right)^* \cdot kx \cdot \sin\frac{\pi x}{a}\,dx$$

where the normalization constant has been brought outside of the integral sign, and $d\tau$ and the integration limits are for the 1-D particle-in-a-box. This integral simplifies to

$$\langle E^{(1)}\rangle = \frac{2k}{a}\int_0^a x \cdot \left(\sin^2\frac{\pi x}{a}\right) dx$$

This integral has a known solution (see the integral table in Appendix 1). Evaluation of this integral specifically is left as an exercise. Substituting for the evaluated integral, this expression becomes

$$\langle E^{(1)}\rangle = \frac{a^2}{4}\cdot\frac{2k}{a} = \frac{ka}{2}$$

Therefore, the energy of the $n = 1$ level is

$$\langle E\rangle = \frac{n^2h^2}{8ma^2} + \frac{ka}{2}$$

b. This is not an exact energy for such a system because the wavefunctions used to determine the energies were the particle-in-a-box wavefunctions, not wavefunctions for a box having a sloped bottom. So although the integral for the perturbation energy is solvable analytically, it does not correct the energy to the *exact* value of the true energy because we are not using the eigenfunctions of the defined system. (Nor are we using the complete Hamiltonian operator for the defined system.) Higher-order perturbation theory, not discussed in this text, may have a better chance of approaching the exact wavefunction and energy eigenvalues for this system.

As the above example shows, although we have defined a first-order *energy* correction, we are still using the ideal forms of the wavefunctions. What we also need is a correction to the *wavefunctions.* It is assumed that, as for the energy correction, the first-order correction to the wavefunction is some correction added to the ideal wavefunction to approximate the real wavefunction:

$$\Psi_{\text{real}} \approx \Psi^{(0)} + \Psi^{(1)} \tag{12.18}$$

It should be understood by now that there is not just one wavefunction for a model system. There are a large number. Many times there are an infinite number of wavefunctions, each with their own quantum numbers. Equation 12.18 can be rewritten to recognize the fact that the many wavefunctions are all different and should be labeled. For example, using the label n (not to be confused with the quantum number!):

$$\Psi_{n,\text{real}} \approx \Psi_n^{(0)} + \Psi_n^{(1)} \tag{12.19}$$

The entire group of wavefunctions for a model system is considered a *complete set* of eigenfunctions. For a model system, the individual wavefunctions are orthogonal; this fact will be important later. Such a situation is analogous to the coordinates x, y, and z defining three-dimensional space: the set (x, y, z) represents a complete set of "functions" used to define any point in space. Any point in 3-D space can be described as the appropriate combination of so many x unit vectors, so many y unit vectors, and so many z unit vectors.*

The complete set of wavefunctions is similar. Such a set can be used to define the complete "space" of a system. The true wavefunction for a real, that is, nonmodel, system can be written in terms of the complete set of ideal wavefunctions, just like any point in space can be written in terms of x, y, and z. Using first-order perturbation theory, any real wavefunction $\Psi_{n,\text{real}}$ can be written as an ideal wavefunction *plus* a sum of contributions of the complete set of ideal wavefunctions $\Psi_m^{(0)}$:

$$\Psi_{n,\text{real}} = \Psi_n^{(0)} + \sum_m a_m \cdot \Psi_m^{(0)} \tag{12.20}$$

where a_m is the coefficient multiplying each ideal $\Psi_m^{(0)}$; they are called *expansion coefficients*. Each real wavefunction $\Psi_{n,\text{real}}$ has a different, unique set of expansion coefficients that define it in terms of the ideal eigenfunctions. A summation like equation 12.20 is called a *linear combination,* because it combines the ideal wavefunctions, which are assumed to be raised to the first power (which defines a linear type of relationship).

Although the process is lengthy, it is algebraically straightforward to determine what the expansion coefficients are for the correction to the nth real wavefunction, $\Psi_{n,\text{real}}$. Recall that each $\Psi_{n,\text{real}}$ is approximated initially by an ideal $\Psi_n^{(0)}$. The m^{th} expansion coefficient a_m for the perturbation to the nth real wavefunction $\Psi_{n,\text{real}}$ can be defined in terms of the perturbation operator $\hat{H}'$, the nth and mth *ideal* wavefunctions $\Psi_m^{(0)}$ and $\Psi_n^{(0)}$, and the energies E_n and E_m of the *ideal* wavefunctions. Specifically,

$$a_m = \frac{\int (\Psi_m^{(0)}) \hat{H}' \Psi_n^{(0)}\, d\tau}{E_n^{(0)} - E_m^{(0)}} \qquad m \neq n \tag{12.21}$$

The restriction $m \neq n$ comes from the derivation of equation 12.21. The integration in the numerator is over the complete space of the system. The requirement that this is nondegenerate perturbation theory also eliminates the possibility that two energies $E_n^{(0)}$ and $E_m^{(0)}$ might be equal due to degenerate wavefunctions. (The extension of perturbation theory to degenerate wavefunctions will not be discussed here.)

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*The unit vectors in the x, y, and z directions are labeled **i**, **j**, and **k**, respectively, so that any point in 3-D space can be represented as $x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$.

Using equation 12.21, the nth real wavefunction $\Psi_{n,\text{real}}$ is written as

$$\Psi_{n,\text{real}} = \Psi_n^{(0)} + \sum_m \left[\frac{\int (\Psi_m^{(0)}) \hat{H}' \Psi_n^{(0)}\, d\tau}{E_n^{(0)} - E_m^{(0)}} \right] \Psi_m^{(0)} \qquad m \neq n \quad \textbf{(12.22)}$$

Note the ordering of the terms having m and n indices in the above equation; it is important to keep them straight. $\Psi_{n,\text{real}}$ is still very similar to the nth ideal wavefunction, but now it is corrected in terms of the other wavefunctions $\Psi_m^{(0)}$ that define the complete set of wavefunctions for the model system. Real wavefunctions defined in this way are not normalized. They must be normalized independently, once the proper set of expansion coefficients has been determined.

The presence of the term $E_n^{(0)} - E_m^{(0)}$ in the denominator of equation 12.22 is very useful. Although this is just a first correction to the wavefunction, in principle equation 12.22 can add an *infinite* number of terms to the wavefunction. However, consider the denominator in the definition of the expansion coefficient. When the difference is small, the value of the fraction—and therefore a_m—is relatively large. On the other hand, if the difference $E_n^{(0)} - E_m^{(0)}$ is large, then the fraction and therefore a_m are small. Negligibly small, sometimes. Consider the four-term linear expansion:

$$\Psi_{0,\text{real}} \approx \Psi_0^{(0)} + 0.95\Psi_1^{(0)} + 0.33\Psi_2^{(0)} + 0.74\Psi_3^{(0)} + 0.01\Psi_4^{(0)}$$

The fourth term in the expansion, $\Psi_{4,\text{ideal}}$, has a very small expansion coefficient. This suggests that either the integral in the numerator of a_4 is very small or that the denominator of a_4 is very large (or both). Either way, little of the approximation is usually lost if that term is simply neglected:

$$\Psi_{0,\text{real}} \approx \Psi_0^{(0)} + 0.95\Psi_1^{(0)} + 0.33\Psi_2^{(0)} + 0.74\Psi_3^{(0)}$$

There is little way of knowing beforehand how large the integral in the numerator of the expression 12.21 will be. Although the ideal wavefunctions $\Psi_m^{(0)}$ and $\Psi_n^{(0)}$ are orthogonal, the presence of the operator $\hat{H}'$ may make the value of the integral nonzero, perhaps even large. But the denominator is in terms of only the energies of the model system, $E_m^{(0)}$ and $E_n^{(0)}$. Since a model system typically has known energy eigenvalues, a good (but not necessarily absolute) rule of thumb is that *if the eigenvalue energies of the wavefunctions are far enough apart, the expansion coefficient will be small.* What this implies is that the most important corrections in the real wavefunction $\Psi_{n,\text{real}}$ will be wavefunctions whose energies are close to the ideal wavefunction $\Psi_n^{(0)}$ of the original wavefunction approximation. So although the complete set of wavefunctions may have an infinite number of ideal wavefunctions, only those that have eigenvalues for energy that are close to the energy of the nth state will have a noticeable impact on the wavefunction correction.

Example 12.10

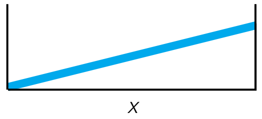
Because of electronegativity differences, the p electron in a bond between two different atoms—say in the $C{\equiv}N^-$ ion—does not act exactly like a particle-in-a-(flat)-box, but like a particle in a box that has a slightly higher potential energy on one side than the other. Assume, then, a perturbation of $\hat{H}' = kx$ for the ground state Ψ_1 of a particle-in-a-box system.

a. Draw the perturbed system.

b. Assuming that the only correction to the real ground-state wavefunction is the second particle-in-a-box wavefunction Ψ_2, calculate the coefficient a_2 and determine the first-order-corrected wavefunction.

Solution

a. The system looks like this:



where the sloped line indicates the true bottom of the box.

b. In order to determine a_2, we need to evaluate the expression

$$a_2 = \frac{\int_0^a \Psi^*_{2,\text{PIAB}} \cdot kx \cdot \Psi_{1,\text{PIAB}}\, dx}{E_{1,\text{PIAB}} - E_{2,\text{PIAB}}}$$

where PIAB stands for particle-in-a-box. The wavefunctions and energies for the particle-in-a-box system are known, so all we need do is substitute for the wavefunctions and the energies.

$$a_2 = \frac{\int_0^a \sqrt{\frac{2}{a}} \sin\frac{2\pi x}{a} \cdot kx \cdot \sqrt{\frac{2}{a}} \sin\frac{1\pi x}{a}\, dx}{\frac{1^2h^2}{8ma^2} - \frac{2^2h^2}{8ma^2}}$$

Since all the functions in the integral are being multiplied together, they can be rearranged (and the constants removed from the integral sign and the denominator simplified) to yield

$$a_2 = \frac{\frac{2k}{a}\int_0^a x \cdot \sin\frac{2\pi x}{a} \cdot \sin\frac{1\pi x}{a}\, dx}{-\frac{3h^2}{8ma^2}}$$

In order to integrate this, we need to substitute the trigonometric identity $\sin ax \cdot \sin bx = \frac{1}{2}[\cos\,(a - b)x - \cos(a + b)x]$ and then use the integral table in Appendix 1. We get:

$$a_2 = \frac{\frac{2k}{a}\left[\frac{1}{2}\int_0^a \left(x\cos\frac{\pi x}{a} - x\cos\frac{3\pi x}{a}\right) dx\right]}{-\frac{3h^2}{8ma^2}}$$

$$= \frac{\frac{k}{a}\left[\frac{a^2}{\pi^2}\cos\frac{\pi x}{a} + \frac{ax}{\pi}\sin\frac{\pi x}{a} - \frac{a^2}{9\pi^2}\cos\frac{3\pi x}{a} - \frac{ax}{3\pi}\sin\frac{3\pi x}{a}\right]\Big|_0^a}{-\frac{3h^2}{8ma^2}}$$

Evaluating this at the limits and simplifying, one finds that

$$a_2 = \frac{128kma^3}{27\pi^2h^2}$$

and so the approximate wavefunction is

$$\Psi_{1,\text{real}} \approx \Psi_{1,\text{PIAB}} + \frac{128kma^3}{27\pi^2h^2} \cdot \Psi_{2,\text{PIAB}}$$

For a cyanide species where the mass is m_e, $k \approx 1 \times 10^{-7}$ kg·m/s^2, and $a \approx 1.15$ Å (that is, 1.15×10^{-10} m), we can evaluate the expression above and get

$$\Psi_{1,\text{real}} \approx \Psi_{1,\text{PIAB}} + 0.1516 \cdot \Psi_{2,\text{PIAB}}$$

A more complete treatment includes contributions from Ψ_3, Ψ_4, and so on, but their contributions become less and less important as the difference between the ideal energies increases. Finally, recall that a_2 for $\Psi_{2,\text{real}}$ (or any other real Ψ) will be different from the a_2 calculated above for $\Psi_{1,\text{real}}$.

12.7 Variation Theory

The second major approximation theory used in quantum mechanics is called *variation theory.* Variation theory is based on the fact that any test wavefunction for a system has an average energy that is equal to or greater than the true ground-state energy of that system. Therefore, the general idea is that *the lower the energy, the better the approximated energy* (and therefore, *the better the wavefunction*). What one does is to suppose a trial wavefunction that has some variable parameter in it, determine the expression for the energy of the system (using the Schrödinger equation or the definition of average energy, $\langle E \rangle$), and then determine what value the variable must have in order to yield the lowest possible energy. Since the wavefunction should also provide average values for other observables, those other values can be determined once a minimum energy is determined for that trial wavefunction.[†] One of the strengths of variation theory is that the trial wavefunctions can be *any* function, as long as the function meets the standards of wavefunctions in general (that is, continuous, integrable, single-valued, and so on) and satisfies any inherent requirement of the system (such as approaching zero as x approaches $\pm\infty$ or the system barriers).

One way of stating the basic idea behind variation theory is the following: for a system having a Hamiltonian operator $\hat{H}$, true wavefunctions Ψ_{true}, and some lowest-energy eigenvalue E_1, the *variation theorem* states that for *any* normalized trial wavefunction ϕ:

$$\int \phi^* \hat{H} \phi \, d\tau \geq E_1 \tag{12.23}$$

If ϕ is identically equal to Ψ_{true} for the ground state, then equation 12.23 is an equality. If ϕ is not *exactly* the ground-state wavefunction, then equation 12.23 is an inequality and the energy produced by the integral is *always greater* than the true ground-state energy of the system. Therefore, the lower the predicted energy, the closer it is to the true ground-state energy and the "better" an energy eigenvalue it is. Proof of variation theory is left as an exercise at the end of this chapter. For an unnormalized wavefunction, equation 12.23 is written as

$$\frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} \geq E_1 \tag{12.24}$$

Usually, the trial wavefunctions have some set of adjustable parameters (a, b, c, . . .). The energy is calculated as an expression in terms of those para-

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[†] However, there is no guarantee that this trial wavefunction will yield accurate values for other observables.

meters, and then the expression is minimized with respect to those parameters. In calculus terms, if the energy is some expression in terms of a single variable $E(a)$, then the minimum energy occurs when the slope of a plot of E versus a is zero:[‡]

$$\left[\frac{\partial E(a)}{\partial a}\right]_{\text{at } a=a_{\text{min}}} = 0$$

and the energy evaluated at this point is the minimum energy:

$$E(a_{\text{min}}) = E_{\text{min}}$$

This minimum energy is the "best" energy that this trial wavefunction can provide. When there are multiple variables in the trial wavefunction, then the absolute minimum with respect to all variables simultaneously is the lowest energy that such a trial wavefunction produces. Although variation theory does provide more complicated expressions for the energies of excited states, the above relatively simple expressions apply only to the ground state of a system.

The trial wavefunctions can have any number of variable parameters, limited mostly by the efficiency in determining the energy minimum. Variation theory is best illustrated by example. We will start by using a trial wavefunction without parameters to show that equation 12.23 is satisfied. For the particle-in-a-box of length a, assume that instead of a sine function, the ground-state wavefunction is instead an upside-down parabola at the center of the box, $a/2$:

$$\phi = ax - x^2$$

This trial wavefunction is shown in Figure 12.8. As you can see, it meets all of the requirements of a wavefunction for a particle-in-a-box system: it is single-valued, continuous, integrable, and goes to zero at the boundaries. To calculate the energy for this trial wavefunction, we need to evaluate

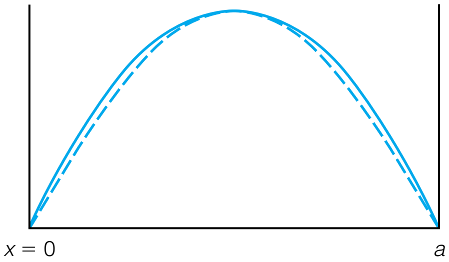

Figure 12.8 Trial wavefunctions for a variation-theory treatment of the ground state of the particle-in-a-box. The solid line is the trial parabolic wavefunction, and the dotted line is the true wavefunction.

$$\int_0^a (ax - x^2)^* \hat{H}(ax - x^2)\, dx$$

where the particle-in-a-box Hamiltonian is $-(\hbar^2/2m)(d^2/dx^2)$. The second derivative of the trial wavefunction is -2, which reduces the integral to

$$\frac{\hbar^2}{m}\int_0^a (ax - x^2)\, dx$$

The expression inside the integral can be integrated, then evaluated between the limits 0 to a. One gets

$$\frac{\hbar^2 a^3}{6m}$$

This trial wavefunction is not normalized, but one can determine the normalization constant to be $\sqrt{30/a^5}$. This makes the predicted energy of the ground state (adjusted by the square of the normalization constant)

$$E_{\text{trial}} = \frac{5\hbar^2}{ma^2} = \frac{5h^2}{4\pi^2 ma^2}$$

This compares with a true energy for the ground state of the particle-in-a-box of $h^2/8ma^2$, or a difference of 1.32%. The approximated energy is *higher* than the true energy by 1.32%.

[‡] Maximum energies also meet this criterion, so it is important to verify that the energy so determined is a minimum, not a maximum.

Example 12.11 shows how variation theory works with a variable that allows one to minimize the energy of a system. It uses the idea that in a multielectron atom, the electrons may not experience the full nuclear charge because of the presence of other electrons. This concept is known as *shielding*. It also illustrates a necessity in approaching higher-level quantum mechanics: the need to be able to evaluate many different types of integrals. A good handbook of integrals and the ability to determine integrals by numerical methods become very helpful when mathematically evaluating even simple problems in quantum mechanics.

Example 12.11

In the helium atom, assume that each electron does not experience the full +2 nuclear charge but instead, due to shielding from the other electron, experiences an effective nuclear charge of Z'. Use Z' as a variable in the form of the hydrogen-like 1*s* orbital to obtain the lowest average energy of helium.

Solution

Using normalized hydrogen-like 1*s* orbitals as trial wavefunctions, the two-electron ϕ is

$$\phi = \frac{Z'^3}{\pi a^3} e^{-Z' r_1/a} e^{-Z' r_2/a}$$

where a has been defined in Chapter 11 as $4\pi\epsilon_0\hbar^2/\mu e^2$. Assuming that the nuclear charge experienced by each electron is Z', the initial Hamiltonian for the helium atom is

$$\left(-\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{Z' e^2}{4\pi\epsilon_0 r_1}\right) + \left(-\frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{Z' e^2}{4\pi\epsilon_0 r_2}\right) + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

However, this Hamiltonian is not complete. If the first electron is experiencing an attractive potential of $Z' e^2/4\pi\epsilon_0 r_1$, then the other electron must be experiencing a potential of $[(2 - Z')e^2]/4\pi\epsilon_0 r_2$. A term like this should appear for both electrons. The complete Hamiltonian is therefore

$$\left(-\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{Z' e^2}{4\pi\epsilon_0 r_1}\right) + \left(-\frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{Z' e^2}{4\pi\epsilon_0 r_2}\right)$$
$$- \frac{(2 - Z')e^2}{4\pi\epsilon_0 r_1} - \frac{(2 - Z')e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

The terms can be rearranged, and the average energy can be calculated. Since we are presuming a one-electron system in the first two parenthetical terms, we can use the energy eigenvalues from the hydrogen atom. We get

$$\langle E_{\text{trial}}\rangle = 2\frac{-Z'^2 e^4 \mu}{8\epsilon_0^2 h^2} + \frac{Z'^6}{\pi^2 a^6} \int e^{-Z' r_1/a} e^{-Z' r_2/a}$$
$$\times \left[-(2 - Z')\frac{e^2}{4\pi\epsilon_0 r_1} - (2 - Z')\frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}\right] e^{-Z' r_1/a} e^{-Z' r_2/a}\, d\tau$$

where $d\tau$ is with respect to electron 1 and electron 2; that is, $d\tau = dr_1\, dr_2$. Using the proper substitutions and manipulations (which will be omitted here), the integral can be evaluated analytically. Its value is

$$\left(-8Z' + \frac{10}{8}Z'\right)\frac{-e^4\mu}{8\epsilon_0^2 h^2}$$

The total energy of the helium atom is therefore

$$\langle E_{\text{trial}}\rangle = 2\frac{-Z'^2e^4\mu}{8\epsilon_0^2h^2} + \left(-8Z' + \frac{10}{8}Z'\right)\frac{-e^4\mu}{8\epsilon_0^2h^2}$$

$$\langle E_{\text{trial}}\rangle = \left(2Z'^2 - 8Z' + \frac{10}{8}Z'\right)\frac{-e^4\mu}{8\epsilon_0^2h^2}$$

where all terms have had the expression $-e^4\mu/8\epsilon_0^2h^2$ factored out. In order for the energy to be a minimum with respect to Z', we must find the value of Z' such that

$$\frac{\partial\langle E\rangle}{\partial Z'} = 0$$

The only part of $\langle E\rangle$ that depends on Z' is the first parenthetical part, so the energy can be minimized by determining when the terms in parentheses are zero. So,

$$\frac{\partial\langle E\rangle}{\partial Z'} = \frac{\partial(2Z'^2 - 8Z' + \frac{10}{8}Z')}{\partial Z'} = 4Z' - 8 + \frac{10}{8} = 0$$

which gives us $Z' = 2 - \frac{5}{16}$. Therefore, the average nuclear charge "felt" by each electron in He according to this model is $\frac{27}{16}$, or just under 2. Now that the effective nuclear charge has been determined, the energy can be evaluated by substituting for all of the constants and Z'. One finds that

$$\langle E_{\text{He}}\rangle = -1.241 \times 10^{-17}\ \text{J}$$

which, compared to -1.265×10^{-17} J determined experimentally, is high by 1.9%. This is slightly better than the perturbation theory treatment presented earlier.

The above example shows two things. First, variation theory *can* provide a more accurate value for the energy of a system. Second, it comes at a cost: a cost of effort. However, using computers to do the calculations, the personal effort can be minimized, so variation theory is particularly well suited for computer applications. In fact, a majority of the effort expended in the modern application of quantum mechanics is in the application of computer programs. Because computers can be programmed with a large number of variables to change in the course of a calculation, variation problems are almost exclusively performed on computers.

We have considered the energy of He using several methods. Table 12.2 summarizes the energies using the different methods we have applied in this chapter, compared with an experimental value. These are not the only methods possible, and you should understand that the methods used here have been used in their simplest forms. But Table 12.2 should give you some idea of the utility of the various tools of quantum mechanics.

Table 12.2 Different energies of the helium atom

E(He) ($\times 10^{-17}$ J)	Method
-1.743	H + H approximation
-1.198	Using perturbation theory, $e^2/4\pi\epsilon_0r_{12}$
-1.241	Using variation theory, effective nuclear charge
-1.265	Experiment

12.8 Linear Variation Theory

Computer-assisted variation theory is especially powerful when there are a large number of variables in the trial function. One of the common ways for this to occur is to assume that the trial function ϕ_i is a linear combination of a set of known functions $\{\Psi_j\}$ called a *basis set:*

$$\phi_i = \sum_j c_{i,j}\Psi_j \tag{12.25}$$

where Ψ_j is an individual *basis function* (for example, a wavefunction of a model system or a function that can easily be integrated) and the $c_{i,j}$ values are the expansion coefficients that must be determined as part of the solution. So not only is the minimum energy not known yet, but neither are the values of the expansion coefficients. As stated earlier, in order to find the lowest energy, the energy must be minimized with respect to all variables simultaneously:

$$\frac{\partial E}{\partial c_{i,1}} = \frac{\partial E}{\partial c_{i,2}} = \frac{\partial E}{\partial c_{i,3}} = \cdots = 0 \tag{12.26}$$

There turns out to be a way to determine not only the energy but also the coefficients. This powerful use of variation theory is called *linear variation theory.*

This form of variation theory is also best illustrated by example. Although the same idea can be applied to a trial wavefunction having any number of terms, a simple example involves the use of a two-term linear combination for the trial wavefunction:

$$\phi_a = c_{a,1}\Psi_1 + c_{a,2}\Psi_2$$

In this example, the basis set $\{\Psi_j\}$ is composed of the two basis functions Ψ_1 and Ψ_2. This form of the trial function can be substituted into equation 12.24 and expanded into several terms, keeping in mind that the ordering of the basis functions is important because of the complex conjugate operation:

$$\frac{\int (c_{a,1}\Psi_1 + c_{a,2}\Psi_2)^* \hat{H} (c_{a,1}\Psi_1 + c_{a,2}\Psi_2)\, d\tau}{\int (c_{a,1}\Psi_1 + c_{a,2}\Psi_2)^* (c_{a,1}\Psi_1 + c_{a,2}\Psi_2)\, d\tau} \geq E_1 \tag{12.27}$$

By making the following simplifying definitions:

$$\begin{aligned} H_{11} &\equiv \int \Psi_1^* \hat{H} \Psi_1 \, d\tau \\ H_{22} &\equiv \int \Psi_2^* \hat{H} \Psi_2 \, d\tau \\ H_{12} = H_{21} &\equiv \int \Psi_2^* \hat{H} \Psi_1 \, d\tau \\ S_{11} &\equiv \int \Psi_1^* \Psi_1 \, d\tau \\ S_{22} &\equiv \int \Psi_2^* \Psi_2 \, d\tau \\ S_{12} = S_{21} &\equiv \int \Psi_2^* \Psi_1 \, d\tau \end{aligned} \tag{12.28}$$

substitutions can be made into equation 12.27 to yield:

$$\frac{c_{a,1}^2 H_{11} + 2c_{a,1}c_{a,2}H_{12} + c_{a,2}^2 H_{22}}{c_{a,1}^2 S_{11} + 2c_{a,1}c_{a,2}S_{12} + c_{a,2}^2 S_{22}} = E_{\text{trial}} \equiv E \geq E_1 \tag{12.29}$$

The H_{ij} integrals are average energy integrals. The S_{ij} integrals are called *overlap integrals.* For orthonormal wavefunctions, the S_{ij} values are either 0 or 1, but in many instances non-orthonormal wavefunctions are used. For simplification, the subscript on the energy is omitted.

The minimization condition represented by equation 12.26 must now be fulfilled according to variation theory. Because of the substitutions made to arrive at equation 12.29, the derivatives with respect to $c_{a,1}$ and $c_{a,2}$ contain a lot of terms but are relatively straightforward to determine. We would find (after substituting for the expression for E itself in the expression for the derivative):

$$\begin{aligned} \frac{\partial E}{\partial c_{a,1}} &= 0 = (H_{11} - ES_{11})c_{a,1} + (H_{12} - ES_{12})c_{a,2} = 0 \\ \frac{\partial E}{\partial c_{a,2}} &= 0 = (H_{21} - ES_{21})c_{a,1} + (H_{22} - ES_{22})c_{a,2} = 0 \end{aligned} \tag{12.30}$$

We get two equations in terms of the coefficients $c_{a,1}$ and $c_{a,2}$, which also have as part of them the energy integrals H_{11}, H_{12} (which equals H_{21}), and H_{22}, and also the overlap integrals S_{11}, S_{12} (which equals S_{21}), and S_{22}. In order for both derivatives to be zero, each of the equations 12.30 must be satisfied at the same time. We must solve these two *simultaneous equations*. You should recognize that we would have more equations to solve simultaneously if we were using an example having more terms, and therefore more constants $c_{i,j}$ in it.

For a set of simultaneous equations that are all equal to zero (like equations 12.30), there are mathematical ways of finding solutions. Linear algebra allows for two possibilities. The first is that all of the constants, in this case $c_{a,1}$ and $c_{a,2}$, are exactly zero. Although this possibility would satisfy the equations 12.30, it provides a useless, or trivial, solution ($\Psi = 0$ exactly: a wavefunction that has been rejected previously for its uselessness). The other possibility can be defined in terms of the coefficients on the *c*'s in equations 12.30, the expressions involving the *H*'s and the *S*'s. Linear algebra allows for a nontrivial solution of the simultaneous equations 12.30 if the determinant formed from the coefficient expressions of equations 12.30 is equal to zero:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \tag{12.31}$$

The above determinant is called a *secular determinant*. Linear variation theory rests on equation 12.31: if the secular determinant formed from the energy and overlap integrals and the energy eigenvalues (which are the unknowns!) is equal to zero, then the equations 12.30 will be satisfied and the energy will be minimized.

There seems to have been a change of focus. First we were concentrating on the coefficients $c_{a,1}$ and $c_{a,2}$, and now we are concerned with a determinant in terms of integrals and energies. This is simply a consequence of linear algebra. Do not be confused by this change in focus. The minimum energy of the system is still the ultimate goal. Recognize, however, that the 2×2 determinant in equation 12.31 can easily be evaluated but will yield an equation that has a term in E^2. Therefore, in solving for E, we will get two answers (using the quadratic formula). The ground-state energy is the lower of the two. Generally, if one has a trial function ϕ_i that has n expansion coefficients, one will get an $n \times n$ secular determinant of the form

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots & H_{2n} - ES_{2n} \\ \dots & \dots & \dots & \dots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \dots & H_{nn} - ES_{nn} \end{vmatrix} = 0 \tag{12.32}$$

where E is the unknown. (Remember, H_{ij} and S_{ij} are the energy and overlap integrals in terms of basis functions. The values of these integrals should be determinable.) In evaluating this determinant one will get a polynomial of order n, in which the highest power of E will be E^n. The polynomial will have up to n solutions of E (some of which may be the same, indicating degenerate wavefunctions). The lowest value of E is our calculated energy of the ground state. Although the focus has shifted abruptly from the determining the coefficients to knowing the energy, we must remember that it is the energy of the system that we are usually most interested in.

If we have the energies, we can determine the coefficients $c_{i,j}$. In the example for a two-term trial function, we will get two energies E_1 and E_2; the lower of the two is the lowest-energy state. Using the simultaneous equations 12.30, it is easy to see that the two coefficients can be expressed as ratios:

$$\frac{c_{a,1}}{c_{a,2}} = -\frac{H_{12} - ES_{12}}{H_{11} - ES_{11}}$$
$$\frac{c_{a,1}}{c_{a,2}} = -\frac{H_{22} - ES_{22}}{H_{21} - ES_{21}} \tag{12.33}$$

where E is the energy of either state. The energy and overlap integrals are calculable, and the energies have already been determined by solving the secular determinant of equation 12.31. Equations 12.33 provide two *ratios* for $c_{a,1}$ and $c_{a,2}$ that should yield the same ratio for each individual value of energy calculated from the secular determinant. The exact values of the coefficients are then adjusted so that ϕ is normalized. If orthonormal basis functions are used, the normalization condition for the approximate wavefunction is easy to express:

$$\sum_j c_{i,j}^2 = 1 \tag{12.34}$$

That is, the sum of the squares of the coefficients must equal 1. After determining the coefficients $c_{a,1}$ and $c_{a,2}$, *the calculation of the ground-state wavefunction is complete* for this example. One also gets the approximate energy and wavefunction for the first excited state. (In general, when one uses n ideal wavefunctions, one determines n linear combinations for the first n energy levels of an approximated system.) These determinations—the energy and the wavefunction of the ground state—are the goals of linear variation theory.

If the basis functions themselves are orthogonal to each other, then the trial wavefunctions determined using variation theory are also orthogonal to each other. Since the trial wavefunction is expressed in terms of a linear combination of other functions and it is the integrals of these other functions that must be evaluated in solving the secular determinant, it is wise to choose such basis functions so that their integrals can easily be evaluated and so that the determinants and coefficients can be determined for any real system. This idea is the main thrust for modern calculational quantum mechanics, which is mostly performed by computer (which can be programmed to perform the various linear algebraic manipulations of a preset trial wavefunction).

Example 12.12

Assume that, for a real system, a real wavefunction is a linear combination of two orthonormal basis functions where the energy integrals are as follows: $H_{11} = -15$ (arbitrary energy units), $H_{22} = -4$, and $H_{12} = H_{21} = -1$. Evaluate the approximate energies of the real system, and determine the coefficients of the expansion:

$$\phi_a = c_{a,1}\Psi_1 + c_{a,2}\Psi_2$$

Solution

According to equation 12.31, the nontrivial solution of the simultaneous equations found by minimizing the energy will be given by

$$\begin{vmatrix} -15 - E \cdot 1 & -1 - E \cdot 0 \\ -1 - E \cdot 0 & -4 - E \cdot 1 \end{vmatrix} = 0$$

where we have explicitly included the facts that, for the orthonormal wavefunctions, $S_{11} = S_{22} = 1$ and $S_{12} = S_{21} = 0$. This secular determinant becomes

$$\begin{vmatrix} -15 - E & -1 \\ -1 & -4 - E \end{vmatrix} = 0$$

which can be expanded to get the quadratic equation

$$E^2 + 19E + 59 = 0$$

Using the quadratic formula, the two possible values of E that will satisfy this equation are

$$E_1 = -15.09 \quad \text{and} \quad E_2 = -3.91$$

What has happened is that one energy level is now slightly lower than the ideal lowest energy level (given by H_{11}) and the other is now slightly higher than the higher of the two ideal energy levels (given by H_{22}). The coefficients $c_{a,1}$ and $c_{a,2}$ can also be evaluated for the lower-energy state (where $E = -15.09$):

$$\frac{c_{a,1}}{c_{a,2}} = -\frac{-1 - (-15.09)(0)}{-15 - (-15.09)(1)} = \frac{1}{0.09}$$

$$0.09c_{a,1} = c_{a,2}$$

So to normalize the wavefunction:

$$\sum_j c_{i,j}^2 = 1 = c_{a,1}^2 + c_{a,2}^2$$

$$c_{a,1}^2 + (0.09c_{a,1}^2) = 1$$

$$c_{a,1} = 0.996$$

and accordingly,

$$c_{a,2} = 0.0896$$

The complete wavefunction for the ground state, where $E = -15.09$ (which is the more negative, or *lower,* energy), is

$$\phi_a = 0.996\Psi_{a,1} + 0.0896\Psi_{a,2}$$

The coefficients for the first excited state are given by using $E = -3.91$ (which is the *higher* of the two energy values) in either of the two ratios in equation 12.33:

$$\frac{c_{a,1}}{c_{a,2}} = -\frac{-4 - (-3.91)(1)}{-1 - (-3.91)(0)} = -\frac{0.09}{1}$$

$$c_{a,1} = -0.09c_{a,2}$$

Normalizing provides the following values for the two coefficients:

$$c_{a,1} = -0.0896 \quad \text{and} \quad c_{a,2} = 0.996$$

The wavefunction whose energy is -3.91 is

$$\phi_a = -0.0896\Psi_{a,1} + 0.996\Psi_{a,2}$$

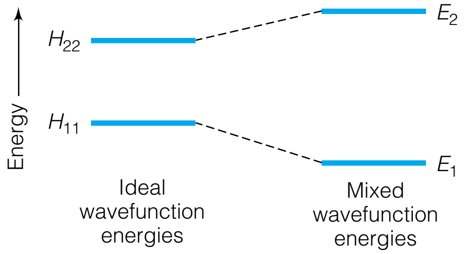

Figure 12.9 A representation of the change in energy values when wavefunctions are mixed. The isolated wavefunction energies, H_{11} and H_{22}, are on the left, and the calculated values for the mixed wavefunction energies, E_1 and E_2, are on the right. The lower ideal energy has gone down slightly, while the higher ideal energy increases.

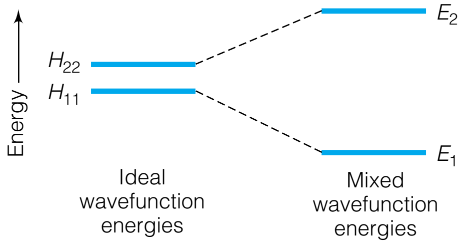

Figure 12.10 When the wavefunctions being mixed are almost degenerate, the separation of the energies upon mixing is much larger than when the energy eigenvalues are far apart. Compare this with Figure 12.9.

Figure 12.9 shows a representation of the energies of the initial basis functions compared to the approximate energies for the linear combination as determined in Example 12.12. The process of taking linear combinations of ideal wavefunctions is sometimes referred to as *mixing* wavefunctions. Note that there has been a slight energy change as the two basis functions combine to yield an approximate wavefunction for a real system. In this case, the energy levels spread further apart when going from the ideal system to the real system approximated by the linear combination of ideal wavefunctions. In all cases of the mixing of two basis functions, the energies spread apart more. The closer in energy the ideal levels, the farther apart they spread. Figure 12.10 illustrates qualitatively how basis functions that are nearly degenerate mix and yield approximate wavefunctions that are now relatively far apart in energy. However, the sum of the energies of the two levels—ideal and approximate—remains the same. (This is true only if basis functions themselves are orthogonal; otherwise, this is not the case.)

Two-level examples are relatively straightforward. In modern computational quantum mechanics, dozens or even hundreds of levels can be calculated using means similar to those described above, although more complex.

12.9 Comparison of Variation and Perturbation Theories

Of the two approximation theories, which one is "better"? As with many such questions, the answer is, it depends. In both cases, the energy can be determined more accurately than the wavefunction. In variation theory, the basis functions can be *anything,* as long as the proposed function fits the requirements of wavefunctions in general and satisfies whatever boundary condition exists. In applications to many large systems, researchers typically use ideal wavefunctions that bear only a slight resemblance to true wavefunctions but that can be integrated easily by computer. [For example, Gaussian-type functions (that is, functions based on e^{-x^2}) are common in variation-theory applications, even though atomic orbitals are not Gaussian functions.] The idea "the lower the energy, the better the energy and the wavefunction" provides a major yardstick for critical evaluation of the wavefunctions by solving the secular determinant. But the functions used in the trial wavefunctions may not make sense in terms of having the form of a true atomic orbital, or may not be easily visualized. Computers are almost irreplaceable in variation-theory calculations, because in order to manipulate a large number of equations, the speed of a computer becomes necessary.

Perturbation theory lacks the guarantee of variation theory. Results from perturbation-theory calculations may yield an energy that can be either higher or lower than the true energy. As such, to a certain extent the predicted energy for a perturbation-theory calculation is always suspect. But the perturbation Hamiltonians $\widehat{H}$ can usually be defined so as to make sense in that their mathematical forms and behaviors are usually well known. For example, common perturbations include electric and magnetic interactions, two- and three-body interactions, dipole-dipole or dipole-induced dipole interactions, or crystal-field interactions—all of which have known mathematical forms and so can easily be included as part of a complete Hamiltonian. Usually, the perturbation wavefunctions also make sense, since many of them are simply corrections to ideal, well-known wavefunctions. Each of the common perturbations listed above can be treated as a separate part of the overall wavefunction, so the complete wavefunction is the sum of many simple parts. Computers are also useful in perturbation theory, especially where the number of perturbations included in a calculation gets large. However, since many of the perturbations are selected because their mathematical behavior is understood, calculation of perturbed energies by hand is not inherently difficult.

Researchers in quantum mechanical calculations should understand the limitations and strengths of each method. Typically, the method used is the one that provides the information a particular researcher wants about a real system. If a well-defined Hamiltonian and wavefunction are desired, then perturbation theory provides that. If the absolute energy is important, variation theory provides a way to get better and better results. The calculational cost is also a factor. Those with access to supercomputers can work with a lot of equations in a relatively short time. Those without may find themselves limited to a small number of corrections to ideal wavefunctions.

An important thing to understand about both of these theories is that when properly applied, they can be used to understand any atomic or molecular system. By using more and more terms in a perturbation-theory treatment or more and better trial functions in variation-theory treatments, one can do approximation calculations that yield virtually exact results. So even though the Schrödinger equation cannot be solved *analytically* for multielectron systems, it can be solved *numerically* using these techniques. The lack of analytic solutions does not mean that quantum mechanics is wrong or incorrect or incomplete; it just means that analytic solutions are not available. *Quantum mechanics does provide tools* for understanding any atomic or molecular system and so it replaces classical mechanics as a way to properly describe electron behavior.

12.10 Simple Molecules and the Born-Oppenheimer Approximation

Since most chemical systems are molecules, it is important to understand how quantum mechanics is applied to molecules. When we use the word *molecule,* we are usually speaking of some chemically bonded system that exists as discrete collections of atoms bonded to each other in some specific way. This contrasts with ionic compounds, which are atoms (or groups of covalently bonded atoms, the so-called polyatomic ions) held together by their opposing charge; that is, they are composed of cations and anions. As one might expect from the previous discussions about wavefunctions in multielectron atoms, wavefunctions of molecules get even more complicated. In reality there are some useful simplifications, which we will get to in the next chapter, but a general consideration of a simple diatomic molecule is useful at this point.

The simplest diatomic molecule is H_2^+, the diatomic hydrogen molecule cation. This system has two nuclei and a single electron. It is illustrated in Figure 12.11, along with definitions of the coordinates used to describe the positions of the particles. Because two nuclei are present, we must consider not only the interaction of the electron with the two nuclei, but also the interaction of the two nuclei with each other. The kinetic energy part of the complete Hamiltonian will have three terms, one for each particle. The potential energy part will also have three terms: an attractive electrostatic potential between the electron and nucleus 1, an attractive electrostatic potential between the

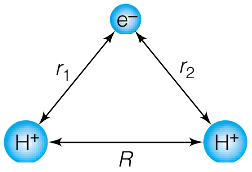

Figure 12.11 Definitions of the coordinates for the H_2^+ molecule.

electron and nucleus 2, and a repulsive electrostatic potential between nucleus 1 and nucleus 2. The complete Hamiltonian for $H_2{}^+$ is

$$\hat{H} = -\frac{\hbar^2}{2m_p}\nabla^2_{p_1} - \frac{\hbar^2}{2m_p}\nabla^2_{p_2} - \frac{\hbar^2}{2m_e}\nabla^2_e - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 R} \tag{12.35}$$

where ∇^2 is the *three*-dimensional spatial second derivative for each of the three particles ($\nabla^2_{p_1}$ refers to the first proton, $\nabla^2_{p_2}$ refers to the second proton, and ∇^2_e refers to the electron). The first two potential energy terms (the fourth and fifth terms in equation 12.35) are the *attractive* potential between the electron and proton 1 and proton 2, respectively (hence the negative signs), and the final term is the *repulsive* potential between the two nuclei (hence the positive sign). The m_p and m_e are the masses of the proton and electron. The distances r_1, r_2, and R are as defined in Figure 12.11.

Figure 12.12 Max Born (1882–1970). Not only did he develop the probabilistic interpretation of the wavefunction, but he also devised a quantum-mechanical description for molecules.

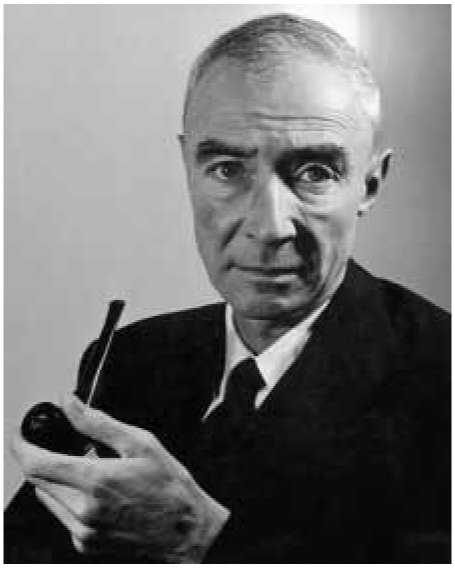

Figure 12.13 J. Robert Oppenheimer (1904–1967). With Born, Oppenheimer helped develop quantum mechanics for application to molecules. Oppenheimer is probably better known, however, for leading the Manhattan Project, which developed the first atomic bombs, during World War II.

As might be expected, no known analytic wavefunctions are eigenfunctions of the Hamiltonian operator in equation 12.35. Some simplifications are needed in order to determine approximate solutions using perturbation or variation theory. One of the complications of this system is that there are now two nuclei, and a proper wavefunction should take into account not only the behavior of the electron but also the behavior of the nuclei. It should be clear that if the relative positions of the nuclei change (for example, during a vibration in which the nuclei are moving alternately closer and farther apart) then the electronic motion will also change to compensate. Any true wavefunction for electrons needs to consider nuclear behavior as well.

However, nuclei are much heavier than electrons (a proton has 1836 times the mass of an electron), so it can be suggested that nuclei move much more slowly than electrons. In fact, it can be assumed that the nuclei move so much more slowly than electrons that for all intents and purposes the motion of an electron can be approximated *as if the nuclei were not moving.* Although the nuclei *are* moving, we treat their motion independently from the motion of the electrons. This statement is called the *Born-Oppenheimer approximation* after Max Born (Figure 12.12) and J. Robert Oppenheimer (Figure 12.13). Born and Oppenheimer's statement is the ultimate basis for *molecular quantum mechanics.*

Mathematically, the Born-Oppenheimer approximation is written as

$$\Psi_{\text{molecule}} \approx \Psi_{\text{nuc}} \times \Psi_{\text{el}} \tag{12.36}$$

which says that the complete molecular wavefunction is the product of a nuclear wavefunction and an electronic wavefunction. This treatment is reminiscent of how we solved the 3-D particle-in-a-box and 3-D rotational motion: separation of variables. The complete Hamiltonian for $H_2{}^+$ can be approximated by two separate Schrödinger equations. The Schrödinger equation for the electronic part is

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2_e - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 R}\right)\Psi_{\text{el}} = E_{\text{el}}\Psi_{\text{el}} \tag{12.37}$$

where R is the internuclear distance and is fixed at some value. Thus, the last term in the parentheses represents, for a given value of R, a *fixed* potential energy value. The Schrödinger equation for the nuclei has the form

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2_{p_1} - \frac{\hbar^2}{2m_e}\nabla^2_{p_2} + E_{\text{el}}(R)\right)\Psi_{\text{nuc}} = E_{\text{nuc}}\Psi_{\text{nuc}} \tag{12.38}$$

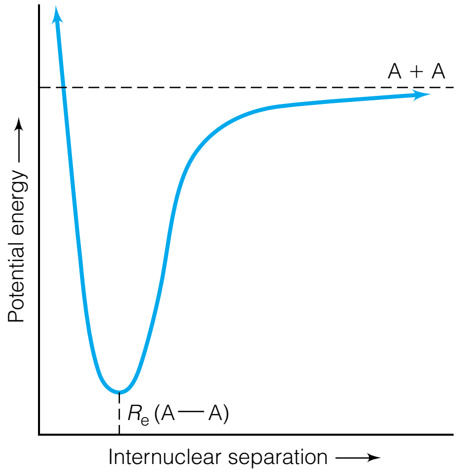

Figure 12.14 A simple potential energy curve for a diatomic molecule A_2. When the nuclei get too close, nuclear repulsion increases quickly. When the nuclei get too far apart, the bond breaks and the molecule separates into two higher-energy A atoms. The minimum-energy internuclear distance, labeled R_e, represents the equilibrium bond distance of the A–A bond in the stable molecule.

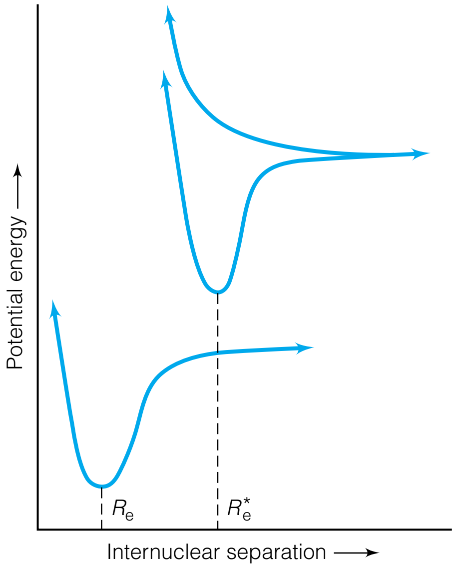

Figure 12.15 A typical set of potential energy curves for the ground state and two excited states of a hypothetical diatomic molecule. The minimum-energy internuclear distance for the excited state, R_e*, is not necessarily the same as the R_e for the ground state. Potential energy diagrams for real molecules are much more complicated than this.

where $\nabla^2_{p_1}$ and $\nabla^2_{p_2}$ are the Laplacian operators for the two nuclei (which are just protons) and $E_{el}(R)$ is the electronic potential energy from the electronic Schrödinger equation, 12.37. These two equations must be solved simultaneously in order to get a complete wavefunction for the molecule.

In the application of the Born-Oppenheimer approximation to diatomic molecules, often the kinetic energy of the nuclei is neglected and the internuclear repulsion is estimated from classical considerations for a particular internuclear distance R (for example, the equilibrium bond distance). This repulsion is included in the potential energy of the electronic Schrödinger part of equation 12.37, which is solved using perturbation or variation techniques. A more complete treatment calculates the internuclear potential at a series of R's and then calculates (numerically) the electronic energy at each R. From this, a plot of electronic energy versus internuclear distance can be constructed, like the one in Figure 12.14. Such a plot is called a *potential energy curve* for the molecule. Figure 12.14 shows a potential energy curve for the ground electronic state, where the energy of the molecule is lowest at the equilibrium bond distance. Each electronic wavefunction, which has its own characteristic energy, will have its own potential energy curve as the internuclear distance changes. Figure 12.15 shows potential energy curves for ground and excited states of a simple diatomic system.

12.11 Introduction to LCAO-MO Theory

The previous section points out that the Born-Oppenheimer approximation is useful in that electronic parts of wavefunctions can be separated from nuclear parts of wavefunctions. However, it does not assist us in determining what the electronic wavefunctions are. Electrons in molecules are described approximately with orbitals just like electrons in atoms are described by orbitals. We have seen how quantum mechanics treats atomic orbitals. How does quantum mechanics treat molecular orbitals? Molecular orbital theory is the most popular way to describe electrons in molecules. Rather than being localized on individual atoms, an electron in a molecule has a wavefunction that extends over the entire molecule. There are several mathematical procedures for describing molecular orbitals, one of which we consider in this section. (Another perspective on molecular orbitals, called valence bond theory, will be discussed in Chapter 13. Valence bond theory focuses on electrons in the valence shell.)

Consider what happens when a molecule is formed: two (or more) atoms combine to make a molecular system. The individual orbitals of the separate atoms combine to make orbitals that span the entire molecule. Why not use this description as a basis for defining molecular orbitals? This is exactly what is done. By using linear variation theory, one can take linear combinations of occupied atomic orbitals and mathematically construct molecular orbitals. This defines the *linear combination of atomic orbitals—molecular orbitals* (LCAO-MO) theory, sometimes referred to simply as *molecular orbital theory.*

In the case of $H_2{}^+$, the molecular orbitals can be expressed in terms of the ground-state atomic orbitals of each hydrogen atom:

$$\phi_{H_2{}^+} = c_1\Psi_{H(1)} + c_2\Psi_{H(2)} \tag{12.39}$$

where $\Psi_{H(1)}$ refers to a ground-state (that is, 1*s*) atomic wavefunction from hydrogen 1, and $\Psi_{H(2)}$ refers to a 1*s* atomic wavefunction from hydrogen 2. Because both hydrogen atoms participate equally in the molecule, it can be argued that the two constants c_1 and c_2 have the same magnitude. It can also be argued that there are two linear combinations are possible, a sum and a difference of the two atomic orbitals (AOs). Therefore, the two atomic orbitals are combining to make two *molecular orbitals* (MOs) having the forms

$$\begin{aligned} \phi_{H_2{}^+,1} &= c_1(\Psi_{H(1)} + \Psi_{H(2)}) \\ \phi_{H_2{}^+,2} &= c_2(\Psi_{H(1)} - \Psi_{H(2)}) \end{aligned} \tag{12.40}$$

Remember that when n atomic orbitals are used, there will be n linearly independent combinations to describe n molecular orbitals. At this point we cannot assume that $c_1 = c_2$. A graphical representation of the sum and difference of the two atomic orbitals is shown in Figure 12.16. Each hydrogen wavefunction is spherically symmetric, although the combination of two atoms makes a system that is no longer spherically symmetric. However, we note that it does have *cylindrical* symmetry, so Figure 12.16 actually represents the magnitudes of the wavefunctions along the axis of a cylinder, which is the internuclear axis of the molecule.

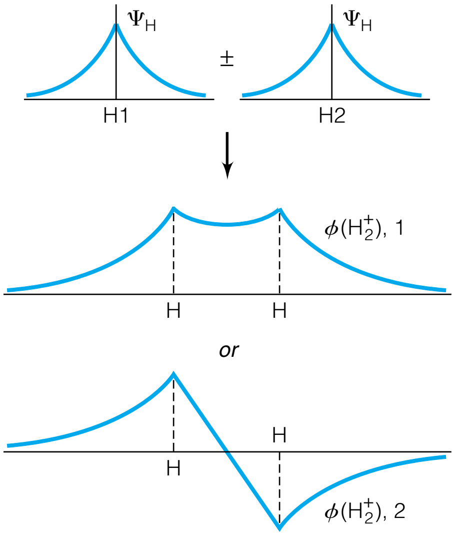

Figure 12.16 Representations of $H_2{}^+$ molecular orbitals from linear combinations of hydrogen atomic orbitals. The MO in the middle plot is the sum of the two AOs at the top, with electron density concentrated between the nuclei. The lower MO is the difference of the two AOs, with electron density concentrated more outside the two nuclei.

Just as in linear variation theory, the coefficients can be determined using a secular determinant. But unlike the earlier examples using secular determinants, in this case some of the integrals are not identically zero or 1 due to orthonormality. In cases where there is an integral in terms of $\Psi^*_{H(1)}\Psi_{H(2)}$ or vice versa, *we cannot assume that the integral is identically zero.* This is because the wavefunctions are centered on different atoms. The orthonormality conditions to this point are only strictly applicable to wavefunctions of the same system. Since the ideal wavefunctions $\Psi_{H(1)}$ and $\Psi_{H(2)}$ are centered on different nuclei, the orthonormality condition does not automatically apply. The solution to the secular determinant will therefore be slightly more complicated.

Because the molecular orbitals must be normalized, we can determine expressions for c_1 and c_2. Normalizing the first equation in 12.40:

$$\int \phi^*_{\mathrm{H_2^+},1}\phi_{\mathrm{H_2^+},1}\,d\tau = 1 = c_1^2\int(\Psi^*_{\mathrm{H}(1)}\Psi_{\mathrm{H}(1)} + 2\Psi^*_{\mathrm{H}(1)}\Psi_{\mathrm{H}(2)} + \Psi^*_{\mathrm{H}(2)}\Psi_{\mathrm{H}(2)})\,d\tau$$

$$1 = c_1^2\left(2 + 2\int \Psi^*_{\mathrm{H}(1)}\Psi_{\mathrm{H}(2)}\,d\tau\right)$$

where the fact that the atomic orbitals on the same atom are normalized has been used for simplification. The integral $\int \Psi^*_{\mathrm{H}(1)}\Psi_{\mathrm{H}(2)}\,d\tau$ involves a wavefunction from each atomic center and, as discussed above, cannot be assumed to be identically zero. This is an example of an overlap integral and is usually given the abbreviation S_{12}. (We defined overlap integrals in our previous discussion of linear variation theory.) The normalization of the molecular wavefunction proceeds as

$$1 = c_1^2(2 + 2S_{12})$$

$$c_1 = \frac{1}{\sqrt{2 + 2S_{12}}} \tag{12.41}$$

By performing a similar normalization, the coefficient for the second molecular orbital can be shown as

$$c_2 = \frac{1}{\sqrt{2 - 2S_{12}}} \tag{12.42}$$

The two coefficients are not the same as long as S_{12} is not zero! The complete wavefunctions are

$$\begin{aligned} \phi_{\mathrm{H_2^+},1} &= \frac{1}{\sqrt{2 + 2S_{12}}}(\Psi_{\mathrm{H}(1)} + \Psi_{\mathrm{H}(2)}) \\ \phi_{\mathrm{H_2^+},2} &= \frac{1}{\sqrt{2 - 2S_{12}}}(\Psi_{\mathrm{H}(1)} - \Psi_{\mathrm{H}(2)}) \end{aligned} \tag{12.43}$$

Now we will evaluate the average energies of these two molecular orbitals for $\mathrm{H_2}^+$. Using the first wavefunction and assuming the purely electronic Hamiltonian where the nuclei are separated at some distance R:

$$E_1 = c_1^2\int(\Psi^*_{\mathrm{H}(1)}\hat{H}\Psi_{\mathrm{H}(1)} + \Psi^*_{\mathrm{H}(1)}\hat{H}\Psi_{\mathrm{H}(2)} + \Psi^*_{\mathrm{H}(2)}\hat{H}\Psi_{\mathrm{H}(1)} + \Psi^*_{\mathrm{H}(2)}\hat{H}\Psi_{\mathrm{H}(2)})\,d\tau$$

(Note the subscripts on each of the Ψ's.) We substitute the following definitions from linear variation theory into the above equation:

$$\begin{aligned} H_{11} = H_{22} &\equiv \int \Psi^*_{\mathrm{H}(1)}\hat{H}\Psi_{\mathrm{H}(1)}\,d\tau = \int \Psi^*_{\mathrm{H}(2)}\hat{H}\Psi_{\mathrm{H}(2)}\,d\tau \\ H_{21} = H_{12} &\equiv \int \Psi^*_{\mathrm{H}(1)}\hat{H}\Psi_{\mathrm{H}(2)}\,d\tau = \int \Psi^*_{\mathrm{H}(2)}\hat{H}\Psi_{\mathrm{H}(1)}\,d\tau \end{aligned} \tag{12.44}$$

These integrals are very similar to those in equation 12.28, except that now wavefunctions from different atoms can interact mathematically. H_{11} and H_{22} are simply the energies of the atomic orbitals. H_{12} and H_{21}, however, represent a sort of energy of mixing of wavefunctions from two different atoms. These integrals are called *resonance integrals.* Integrals of this sort—where one Ψ comes from one atomic center and the other Ψ comes from another atomic center—are not predicted by classical mechanics and are of purely quantum-mechanical origin. The equalities in equation 12.44 arise from the fact that both atoms are hydrogens. If this were a heteronuclear diatomic system, each resonance integral H_{11}, H_{12}, H_{21}, and H_{22} would have its own independent definition.

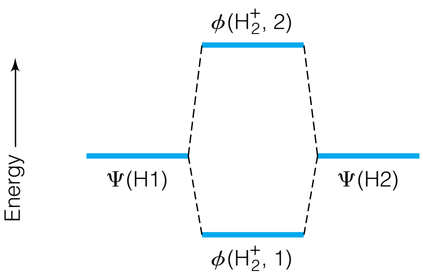

Figure 12.17 When the AOs of two hydrogen atoms combine to make MOs of $H_2{}^+$, the antibonding orbital increases in energy slightly more than the bonding orbital decreases in energy. (The energy axis is not to scale.) Expressions like equations 12.42–12.44 can be used to estimate the differences between atomic and molecular orbital energies.

With the substitutions, the expressions for the average energies become

$$E_1 = \frac{H_{11} + H_{12}}{1 + S_{12}} \qquad E_2 = \frac{H_{22} - H_{12}}{1 - S_{12}} \tag{12.45}$$

where E_1 is less than E_2. Curiously, the sum of molecular orbital energies E_1 and E_2 is not the same as the sum of the two original atomic orbital energies. The total energy depends on the magnitudes of H_{12} and S_{12}; in the case of $H_2{}^+$, the sum of the two orbital energies has increased slightly. This is illustrated in Figure 12.17. The *total* energy of the system includes not just the energy of the orbitals but the repulsive energy due to the two nuclei at some distance R. This total energy must therefore be evaluated to minimize the energy in terms of R, H_{12}, and S_{12}. The resonance and overlap integrals can be evaluated analytically using elliptical polar coordinates (instead of spherical polar coordinates).* The expressions one obtains for the integrals upon application of elliptical polar coordinates are

$$H_{12} = E_{11}S_{12} + 2E_{11}e^{-R/a_0}\left(1 + \frac{R}{a_0}\right) \tag{12.46}$$

$$S_{12} = e^{-R/a_0}\left(1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2}\right) \tag{12.47}$$

where E_{11} is simply the energy of the atomic hydrogen 1*s* orbital and a_0 is the first Bohr radius, 0.529 Å. The only remaining parameter is R. By varying R and calculating the energy, we can find the internuclear distance at which the energy is minimized. When this is done, an R of 1.32 Å and an energy of -2.82×10^{-19} J with respect to H + H$^+$ are calculated. (The energy of infinitely separated H + H$^+$ is arbitrarily set equal to zero. Our result means that the $H_2{}^+$ system is calculated as being 2.82×10^{-19} J lower in energy than the two separated atoms, meaning that it is more stable by that amount.) This can be compared to experimentally determined properties of $R = 1.06$ Å and $E = -4.76 \times 10^{-19}$ J (relative to H + H$^+$). Not bad for a first approximation.

Example 12.13

Comment on the value of S_{12} as the interatomic distance R goes from 0 to ∞.

Solution

When R is zero, the two nuclei essentially represent a single atom of charge 2+. Due to orthonormality considerations, the overlap integral S_{12} should be equal to 1. As the two nuclei separate, they get farther and farther apart and the ground-state atomic wavefunctions overlap less and less. At $R = \infty$, each atom is effectively isolated from the other and the overlap integral should essentially be 0. At intermediate distances, S_{12} can have any value between 0 and 1. This analysis does illustrate why S_{12} is called an overlap integral. It indicates a relative amount of overlap between the atomic orbitals.

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*In fact, $H_2{}^+$ is a system that can be solved analytically if the Born-Oppenheimer approximation is imposed on the system first. Otherwise, it is not analytically solvable.

Example 12.14

Using $R = 1.32$ Å, evaluate S_{12}, H_{12}, E_1, E_2, and the wavefunctions for $H_2{}^+$. Use -13.60 eV as the value for the energy of a 1*s* hydrogen electron, and express answers in units of eV. (An electron volt, or eV, equals 1.602×10^{-19} J and is a useful unit for atomic-scale values of energy.)

Solution

Since both R and a_0 are in units of Å, it is unnecessary to consider any unit conversions. Using the expressions above,

$$S_{12} = e^{-1.32\text{Å}/0.529\text{Å}}\left[1 + \frac{1.32\text{ Å}}{0.529\text{ Å}} + \frac{(1.32\text{ Å})^2}{3(0.529\text{ Å})^2}\right] = 0.459$$

$$H_{12} = (-13.60\text{ eV})(0.459) + 2(-13.60\text{ eV}) \cdot e^{-1.32\text{Å}/0.529\text{Å}}\left(1 + \frac{1.32\text{ Å}}{0.529\text{ Å}}\right)$$
$$= -14.08\text{ eV}$$

$$E_1 = \frac{-13.60\text{ eV} - 14.08\text{ eV}}{1 + 0.459} = -18.97\text{ eV}$$

$$E_2 = \frac{-13.60\text{ eV} - (-14.08\text{ eV})}{1 - 0.459} = +0.887\text{ eV}$$

The wavefunctions that have these energies are

$$\phi_{H_2{}^+,1} = 0.585(\Psi_{H(1)} + \Psi_{H(2)})$$
$$\phi_{H_2{}^+,2} = 0.961(\Psi_{H(1)} - \Psi_{H(2)})$$

12.12 Properties of Molecular Orbitals

Consider the wavefunctions determined for the MOs of $H_2{}^+$. Although they are very simple molecular orbitals, they do have certain characteristics that can be used to describe all molecular orbitals. Figure 12.18 shows a representation of the sum and difference of the two atomic H orbitals and their squares. Since the probability that the electron will exist in a region is proportional to the square of the wavefunction, Figure 12.18b indicates the probability for an electron existing in the molecule. Since the system is cylindrical, so is the probability (this is similar to our discussion of radial shell probabilities for the hydrogen atom). In the lower-energy wavefunction (Figures 12.18a and b), the probability of the electron in the cylindrical volume *between* the two nuclei has increased relative to the original, separate atomic wavefunctions. Since the two positive nuclei would otherwise repel each other, this increase in electron probability or electron density serves to lower the repulsion between the nuclei and stabilize the entire molecular system; that is, it lowers the energy. Any molecular orbital whose energy is lower than the energy of the separated atomic orbitals is called a *bonding orbital.*

The higher-energy molecular orbital (Figures 12.18c and d), on the other hand, concentrates more electron probability in a cylindrical volume *outside* the two nuclei. An electron in this orbital would therefore have a decreased probability of being found between the nuclei, and the repulsion between positively charged nuclei would increase, destabilizing the overall system. Any molecular orbital whose energy is higher than the energy of the separated atomic orbitals is called an *antibonding orbital.* This antibonding orbital has a

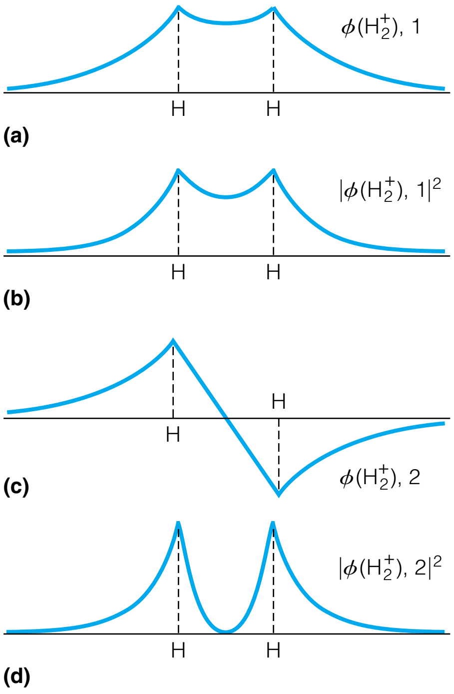

Figure 12.18 Radial plots of the molecular orbitals and their probabilities for $H_2{}^+$. For the bonding orbital (a), there is an increased probability for the electrons between the nuclei (b). For the antibonding orbital (c), there is a decreased probability between the nuclei (d). The antibonding orbital shows a node between the two nuclei.

nodal surface between the nuclei; the electron's probability of being at that point is exactly zero. If all atomic orbitals were assumed to combine to make molecular orbitals, half of the molecular orbitals would be bonding and half would be antibonding orbitals. (There are also *nonbonding orbitals* that do not contribute to molecular bonding, but they will not be considered at this point.) One useful definition is bond order. If the number of electrons in bonding orbitals were n_{bond} and the number of electrons in antibonding orbitals were n_{antibond}, the *bond order* n is

$$n = \frac{n_{\text{bond}} - n_{\text{antibond}}}{2} \tag{12.48}$$

Bond order is qualitatively related to the strength and number (that is, single, double, triple) of bonds between atoms in a molecule.

It has been assumed that our system and our orbitals are cylindrically symmetric. This makes sense, because our molecular orbitals were spherical to start with and the combination of two spheres yields a shape that is cylindrical about the line connecting the two nuclei. A cylindrical wavefunction has a magnitude that is symmetric about some axis, in this case defined by the line drawn directly between the two nuclei. Such a line is often used to indicate a bond. Any orbital whose behavior or magnitude is cylindrical about the bond between the two atoms is called a *sigma* (σ) *orbital*. The combination of the two atomic wavefunctions in H_2^+ therefore yields one bonding sigma orbital (denoted σ) and one antibonding sigma orbital (denoted σ^*). Figure 12.19 shows a labeled molecular orbital diagram for the two molecular orbitals of H_2^+.

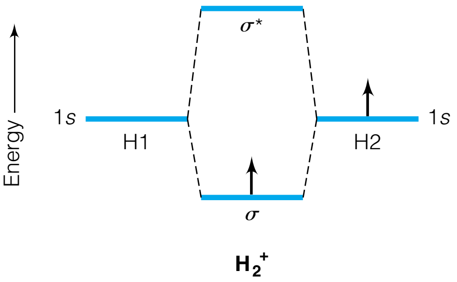

Figure 12.19 A molecular orbital diagram for H_2^+, showing the σ and σ^* labels for the molecular orbitals. (Compare this to Figure 12.17.) In the ground state, the single electron occupies the lowest-energy molecular orbital. Since this represents a lowering of the energy with respect to the energy of the atoms, the molecule is more stable than the separated atoms.

Since the σ orbital for H_2^+ has a lower energy than the two individual orbitals of the separated H atoms, if an electron were residing in that orbital, the overall energy of the molecular system would be lowered. Lower energies are more stable, and so the H_2^+ system would be considered energetically stable in its ground state. Although it requires special conditions to generate, H_2^+ is a stable species relative to separated $H + H^+$. Because there is one electron in a bonding orbital and none in an antibonding orbital, the bond order of H_2^+ is $\frac{1}{2}$. This also implies that a bond exists and that the species would be stable. If, however, the electron in H_2^+ were to absorb energy and be promoted into the antibonding orbital, repulsion between nuclei would be increased and the molecule should break apart into the stabler $H + H^+$ species. This is indeed what happens experimentally.

12.13 Molecular Orbitals of Other Diatomic Molecules

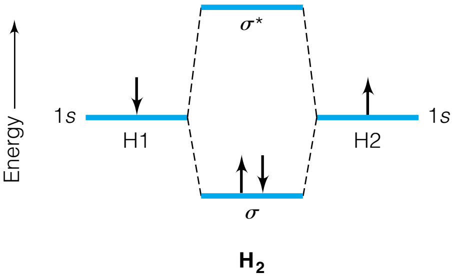

Figure 12.20 A qualitative molecular orbital diagram for H_2 is very similar to that of H_2^+, except for the presence of the second electron with a spin opposite that of the first.

The concept of molecular orbitals can be extended to diatomic molecules larger than the H_2^+ system. By including a second electron, we can consider the neutral hydrogen molecule, H_2. For the ground electronic state, we can borrow the molecular orbital diagram for H_2^+, which has a single electron in the bonding σ orbital. The second electron in H_2 also resides in this orbital, but its spin must be opposite the spin of the first electron to satisfy the Pauli exclusion principle. The MO diagram for H_2 is shown in Figure 12.20.

The approximate wavefunction for H_2 is similar to that for the He atom in that there are now two electrons that need spatial functions, and the overall spin-orbital wavefunction must be antisymmetric with respect to exchange of the two electrons. Recall that the wavefunction for the electron in the bonding orbital of $H_2{}^+$, from equation 12.43, is

$$\phi_{H_2{}^+,1} = \frac{1}{\sqrt{2 + 2S_{12}}}(\Psi_{H(1)} + \Psi_{H(2)})$$

The other wavefunction from equation 12.43 is for the antibonding orbital. Since both electrons can be described with this spatial wavefunction, the spatial wavefunction for the H_2 molecule is the product of two such ϕ's:

$$\phi_{H_2} = \frac{1}{2 + 2S_{12}}[\Psi_{H(1)}(\text{el.}1) + \Psi_{H(2)}(\text{el.}1)][\Psi_{H(1)}(\text{el.}2) + \Psi_{H(2)}(\text{el.}2)] \tag{12.49}$$

where each linear combination has been labeled as referring to electron 1 or electron 2 (el.1 or 2). This spatial wavefunction must be multiplied by the antisymmetric spin function $1/\sqrt{2}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$ to get the complete wavefunction that satisfies the Pauli principle (that is, is antisymmetric). The complete wavefunction is

$$\begin{aligned}\phi_{H_2} = \frac{1}{\sqrt{2}}\frac{1}{2 + 2S_{12}}&[\Psi_{H(1)}(\text{el.}1) + \Psi_{H(2)}(\text{el.}1)] \\ &\times [(\Psi_{H(1)}(\text{el.}2) + \Psi_{H(2)}(\text{el.}2)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]\end{aligned} \tag{12.50}$$

The average energy of this wavefunction can also be evaluated versus R under the Born-Oppenheimer approximation. We can calculate that, with respect to two separated H atoms, the decrease in energy upon bonding is 4.32×10^{-19} J for the hydrogen molecule (compared to 7.59×10^{-19} J experimentally), at a minimum-energy R of 0.85 Å (compared to 0.74 Å experimentally). The calculated bond order of H_2 is 1, corresponding to the existence of a single bond.

Because both electrons reside in the σ bonding orbital, an "electron configuration" of σ^2 can be used to describe the ground electronic state of H_2. (Because H_2 is a homonuclear diatomic molecule, we add a subscript "g" to the label—σ_g^2—to indicate the orbital's symmetry property with respect to the center of the molecule. Electrons in the antibonding orbital are labeled σ_u^*, the "u" also referring to the orbital's symmetry properties.[†] Symmetry will be discussed in the next chapter.) To emphasize that the electrons in the σ orbital derive from 1*s* electrons from H atoms, the more detailed $(\sigma_g 1s)^2$ label can also be used.

Larger atoms have more occupied atomic orbitals that can combine into molecular orbitals. It is common to use the second row of atoms, Li through Ne, to illustrate the principles. For diatomics having electrons originating from different atomic electronic shells, we adopt the approximation that *only atomic orbitals of similar energies will combine to make molecular orbitals.*

Thus, for Li_2, the 1*s* orbital from one Li atom will interact with the 1*s* orbital from the other Li atom, as we saw occurring in H_2. Additionally, the 2*s* orbital of the first Li atom will interact with the 2*s* orbital of the second Li atom, creating another bonding and antibonding pair of molecular orbitals. The four 1*s* electrons will fill the $\sigma_g 1s$ and $\sigma_g^* 1s$ molecular orbitals, and the two

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[†] The labels "g" and "u" stand for the German words *gerade* and *ungerade,* respectively.

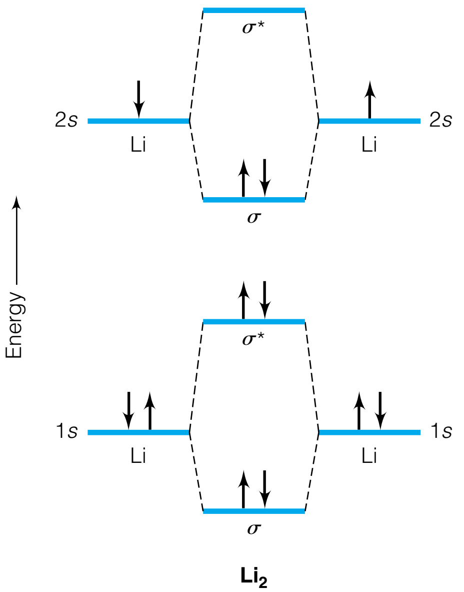


Figure 12.21 A molecular orbital diagram for Li$_2$, showing that $1s$ atomic orbitals interact with $1s$ orbitals, and $2s$ orbitals interact with $2s$ orbitals. Although this is an additional approximation, it helps us understand the wavefunctions of these simple molecules.

$2s$ electrons will occupy the $\sigma_g 2s$ bonding molecular orbital (and have opposite spins). A molecular orbital diagram for Li$_2$ is shown in Figure 12.21.

Example 12.15

Borrowing from the molecular electron configuration of H$_2$, what is the electronic configuration of Li$_2$?

Solution

Since we have two electrons in the $\sigma_g 1s$ molecular orbital, two electrons in the $\sigma_g^* 1s$ antibonding orbital, and two electrons in the $\sigma_g 2s$ molecular orbital, the electron configuration is

$$(\sigma_g 1s)^2(\sigma_g^* 1s)^2(\sigma_g 2s)^2$$

Note that sigma orbitals arise from the combination of the $2s$ atomic orbitals as well.

When p orbitals participate in making molecular orbitals, a new consideration arises. Because of the directionality of the p orbitals, there are two possibilities when p orbitals combine. One p orbital from each atom (arbitrarily the p_z orbital) can combine in a head-on, axial fashion (Figure 12.22a). The other two p orbitals (p_x and p_y) must combine in a side-on, off-axis fashion (Figure 12.22b). Although the two side-on-overlapping p combinations are degenerate, these molecular orbitals do *not* have the same energy as the axially overlapping molecular orbital. The axially overlapped molecular orbital, with increased electron density within the internuclear axis, is also a σ orbital; bonding and antibonding σ orbitals are also produced by this combination of two p atomic orbitals.

The four side-on-overlapping p orbitals make *pi* (π) *molecular orbitals,* whose electron densities exist outside the intermolecular axis. (In fact, the internuclear axis represents a node for π orbitals.) The combination of the four p atomic orbitals produces two degenerate bonding π orbitals and two degen-

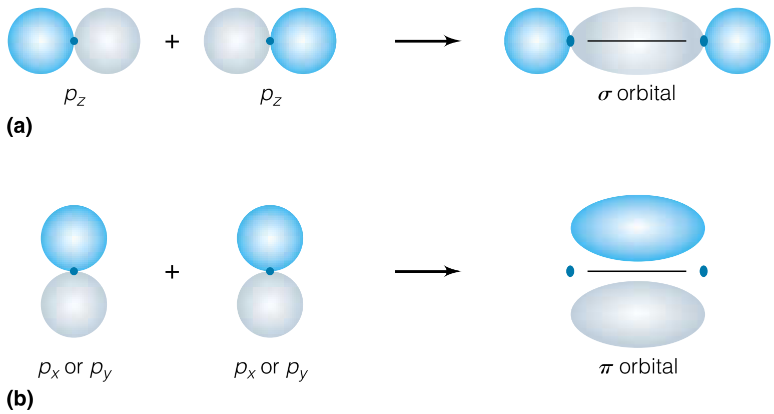


Figure 12.22 (a) The p_z atomic orbitals interact head-on, yielding σ bonding and antibonding orbitals. (b) The p_x and p_y atomic orbitals interact in a side-on fashion, yielding π orbitals whose electron density is outside the internuclear axis. The different shades of the lobes indicate different phases of the wavefunctions.

erate antibonding π orbitals. (In filling degenerate π orbitals, Hund's rules still apply.) Because of their symmetry properties, bonding π orbitals have the "u" label and antibonding π orbitals have the "g" label for homonuclear diatomics.

The relative energy ordering of σ and π molecular orbitals from p atomic orbitals depends on the second-row atoms involved. For Li_2 through N_2, the ordering is $(\pi_u 2p_x, \pi_u 2p_y) < \sigma_g 2p_z < (\pi_g^* 2p_x, \pi_g^* 2p_y) < \sigma_u^* 2p_z$. For O_2 and F_2 (and Ne_2, although this species does not exist as a stable molecule), the ordering of the bonding molecular orbitals is switched: $\sigma_g 2p_z < (\pi_u 2p_x, \pi_u 2p_y) < (\pi_g^* 2p_x, \pi_g^* 2p_y) < \sigma_u^* 2p_z$. How can we justify the difference in ordering of molecular orbitals? First of all, we note that for the smaller atoms, the $2s$ and $2p$ orbitals are closer in energy than they are for the larger atoms of the second-row atoms. By the reasoning above that only similar-energy atomic orbitals will interact, the smaller atoms will have more interaction between the $2s$ orbitals and the $2p$ orbitals than the larger atoms. Because of that increased interaction, one resulting molecular orbital increases its energy and the other molecular orbital decreases its energy. In addition, not all three pairs of the $2p$-derived molecular orbitals will interact strongly with the $2s$ orbital—their orientations aren't right for good interaction. (This is a consequence of symmetry, which will be discussed in the next chapter.) Only one of the molecular orbitals has the correct orientation and will interact, altering its expected energy. This ultimately yields a relative ordering of molecular orbitals for Li_2 through N_2 that differs from that in O_2 through Ne_2.

Perhaps the most obvious experimental observation in support of this model of molecular wavefunctions is the diamagnetism of O_2, caused by one unpaired electron in each of the two degenerate π_g^* molecular orbitals. Figure 12.23 summarizes the occupancies of the molecular orbitals for diatomics of the second-row elements.

For heteronuclear diatomics, the molecular orbital picture is similar, although the energies of the atomic orbitals are no longer the same. Molecular orbital diagrams show atomic orbitals at different levels on the vertical energy scale, as shown in Figure 12.24 for NO and HF. Note in HF that two of the originally degenerate p atomic orbitals of F do not participate in the bonding (by this approximation). Thus, they remain in doubly degenerate nonbonding orbitals. The electron configuration of HF, $(\sigma)^2(2p_x^2, 2p_y^2)$, does not have atomic orbital labels for the doubly occupied bonding σ orbital making the internuclear bond. In this case, it is derived from the $1s$ atomic orbital of H and the $2p_z$ atomic orbital of F.

12.14 Summary

Spin has dramatic consequences for the electronic structure of atoms. Because of the Pauli principle, at most two electrons can fit in each orbital. Given the restrictions on the ℓ and m_ℓ quantum numbers, this requires that successive shells about atoms be filled with successive electrons. This gives atoms *size*. If the Pauli principle did not apply to electrons, they could all fit into a $1s$ H-like orbital. But because only two of them can be allowed in each orbital, one of each spin, larger and larger shells must be filled as the number of electrons increases. Ultimately, the Pauli principle gives atoms their size.

There are no known analytic solutions to the Schrödinger equation for systems more complex than the hydrogen atom. This does not imply that quantum mechanics is not applicable to larger systems. Perturbation theory

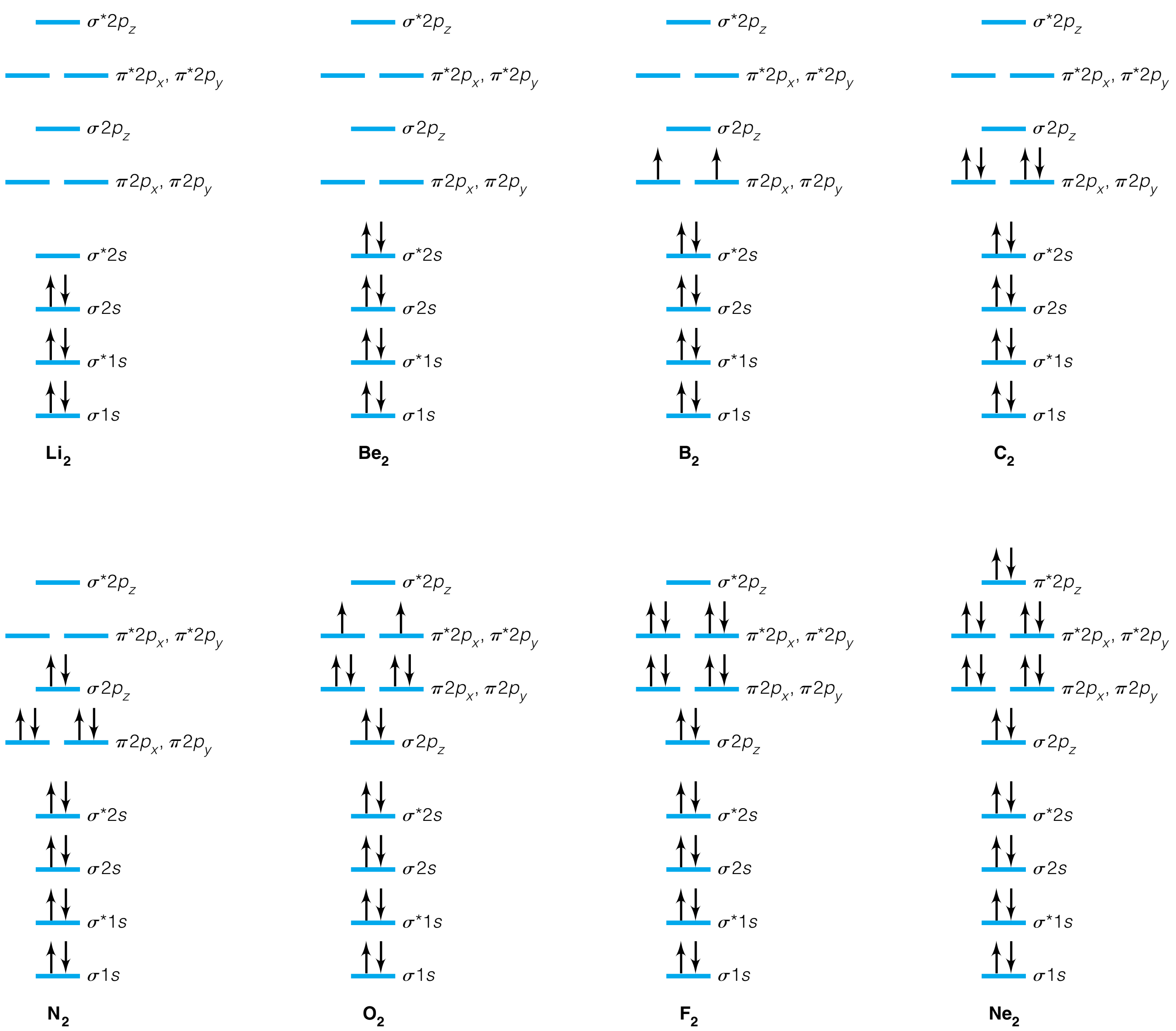


Figure 12.23 Molecular orbitals of Li_2 through F_2. The energy axis is not to scale, but this diagram should provide an idea of how the molecular orbitals are ordered and filled with electrons for these homonuclear diatomic molecules.

and variation theory are two tools used in quantum mechanics to approximate the behavior and energy of multielectron systems. Application of either approximation technique can in principle yield energy eigenvalues as close to experiment as desired. Recall that this is the true test of a theory: how well it reproduces and explains experiment (as with the discovery of antimatter, predicted by Dirac's relativistic quantum mechanics. Such agreement between theory and experiment fosters confidence in both). Depending on how one approaches a system, one can devise a numerical understanding of electron behavior. We will also find in the next few chapters how quantum mechanics can be applied to behavior of not just electrons, but of molecules as a whole.

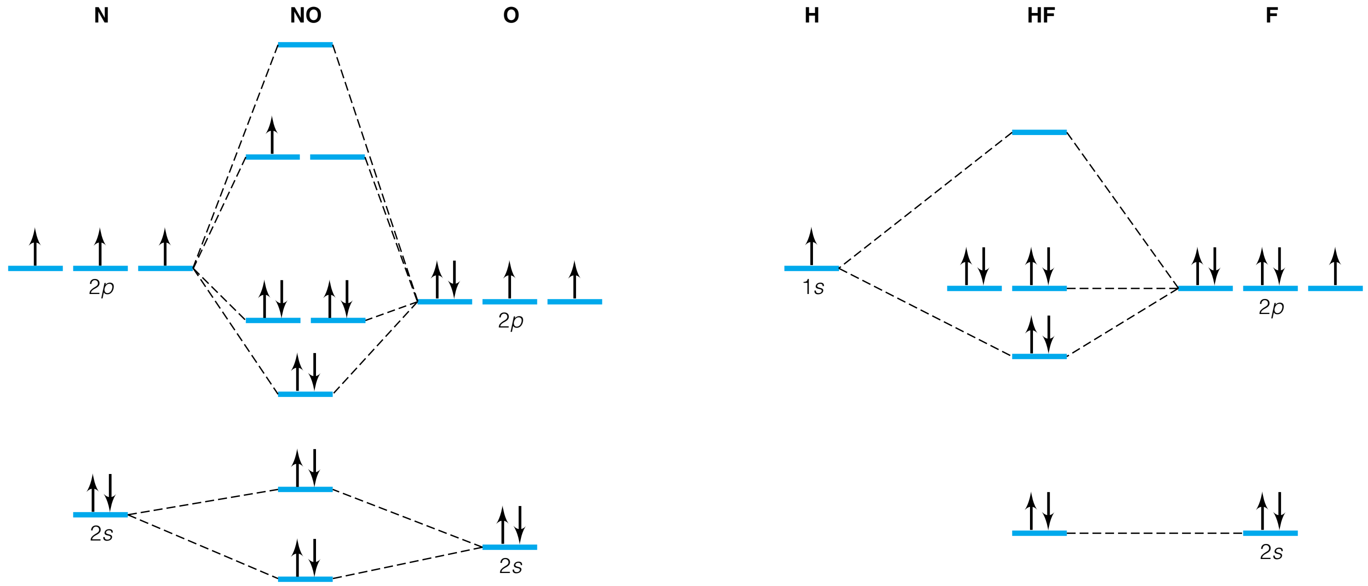


Figure 12.24 Molecular orbitals of the heteronuclear diatomic molecules NO and HF. The energy axis is not to scale, and only the valence shell electrons are shown. Compare these diagrams with those in Figure 12.23.

Our understanding of molecular quantum mechanics begins with molecular orbitals, which are based on atomic orbitals. As with many tools used to describe nature, we started at the bottom and are working our way up. The fundamentals of molecular quantum mechanics provide us with the tools to understand most of matter, at least as we understand it today. The next few chapters broaden the applications of quantum mechanics to molecular systems.

12.2 Spin

12.1. In the Stern-Gerlach experiment, silver atoms were used. This was a good choice, as it turned out. Using the electron configuration of silver atoms, explain why silver was a good candidate for being able to observe the intrinsic angular momentum of the electron. (*Hint:* Don't use the aufbau principle to determine the electron configuration of Ag, because it's one of the exceptions. Look up the exact electron configuration in a table.)

12.2. Using α and β labels, write two possible wavefunctions for an electron in the $3d_{-2}$ orbital of He^+.

12.3. Antimatter and matter destroy each other, giving off electromagnetic radiation as the total mass of the particles is converted to energy. Using Einstein's matter-energy equivalence equation $E = mc^2$, calculate the number of joules of energy given off when **(a)** one electron and one positron destroy each other (the mass of the positron is the same as the mass of the electron), and **(b)** 1 mole of electrons destroys 1 mole of positrons.

12.4. Are the two spin functions α and β orthogonal? Why or why not?

12.5. **(a)** Differentiate between the quantum numbers s and m_s. **(b)** What will the possible values of m_s be for a particle having an s quantum number of 0, 2, and $\frac{3}{2}$?

12.3 He Atom

12.6. Are mathematical expressions for the following potential energies positive or negative? Explain why in each case. **(a)** The attraction between an electron and a helium nucleus **(b)** The repulsion between two protons in a nucleus **(c)** The attraction between a north and a south magnetic pole **(d)** The force of gravity between the sun and Earth **(e)** A rock perched on the edge of a cliff (with respect to the base of the cliff)

12.7. Write out the complete Schrödinger equation for Li and indicate what terms in the operator make the equation unsolvable exactly.

12.8. **(a)** Assume that the electronic energy of Li was a product of three hydrogen-like wavefunctions with principal quantum number equal to 1. What would be the total energy of Li?

(b) Assume that two of the principal quantum numbers are 1 and the third principal quantum number is 2. Calculate the estimated electronic energy.

(c) Compare both energies with an experimental value of 3.26×10^{-17} J. Which estimate is better? Is there any reason you might assume that this estimate would be better from the start?

12.4 Spin Orbitals; Pauli Principle

12.9. Spin orbitals are products of spatial and spin wavefunctions, but correct antisymmetric forms of wavefunctions for multielectron atoms are sums and differences of spatial wavefunctions. Explain why acceptable antisymmetric wavefunctions are sums and differences (that is, combinations) instead of *products* of spatial wavefunctions.

12.10. Show that the correct behavior of a wavefunction for He is antisymmetric by exchanging the electrons to show that $\Psi(1, 2) = -\Psi(2, 1)$.

12.11. Use a Slater determinant to determine the correctly behaved wavefunction for the ground state Li^+.

12.12. Why does the concept of antisymmetric wavefunctions not need to be considered for the hydrogen atom?

12.13. **(a)** Construct Slater determinant wavefunctions for Be and B. (*Hint:* Although you need only include one p orbital for B, you should recognize that up to six possible determinants can be constructed.)

(b) How many different Slater determinants can be constructed for C, assuming that the p electrons spread out among the available p orbitals and have the same spin? How many different Slater determinants are there for F?

12.14. Examples in the chapter suggest that the number of terms in a proper antisymmetric wavefunction given by a Slater determinant is $n!$, where n is the number of electrons and ! implies the factorial of n ($n! = 1 \cdot 2 \cdot 3 \cdot 4 \cdot \cdots \cdot n$). Coming up with the correct terms for a proper wavefunction becomes a difficult task very quickly; hence the extreme simplicity provided by a Slater determinant.

(a) Verify the $n!$ relationship for the examples of He, Li, and Be given in the text. (*Hint:* you may have to review rules for evaluating determinants.)

(b) Determine the number of terms in an antisymmetric wavefunction for C, Na, Si, and P.

12.5 Aufbau Principle

12.15. Using a periodic table (or Table 12.1), find the elements whose electron configurations do not follow the aufbau principle strictly. Comment on any relationship between these elements or their place within the periodic table.

12.16. Label each electron configuration for the listed atom as a ground state or an excited state. **(a)** Li, $1s^2\ 2p^1$ **(b)** C, $1s^2\ 2s^2\ 2p^2$ **(c)** K, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4p^1$ **(d)** Be, $1s^2\ 3s^2$ **(e)** U (outer shells only) $7s^2\ 5f^3\ 7p^1$

12.17. For each atomic state in exercise 12.16, determine how many possible ways the electrons in the outermost shell can occupy spin orbitals and satisfy Hund's rule, and list them explicitly. For example, in the case of Li, the outermost shell has three more specific possibilities: $2p_x^1$ (spin α or spin β), or $2p_y^1$ (spin α or spin β), or $2p_z^1$ (spin α or spin β), for a total of six possibilities.

12.6 Perturbation Theory

12.18. In deriving equation 12.17, we stated that the correction to the energy is an approximation. Why can't we simply assume that the integral representing the first-order correction can be solved analytically, and therefore be exact?

12.19. An *anharmonic* oscillator has the potential function $V = \frac{1}{2}kx^2 + cx^4$, where c can be considered a sort of *anharmonicity constant.* Determine the energy correction to the ground state of the anharmonic oscillator in terms of c, assuming that $\widehat{H}°$ is the ideal harmonic oscillator Hamiltonian operator. Use the integral table in Appendix 1 in this book.

12.20. Why would a perturbation $\widehat{H}' = cx^3$ not work for an energy correction to a ground-state harmonic oscillator? (*Hint:* try evaluating the energy explicitly, then consider how to arrive at the answer without evaluating the integral.)

12.21. Calculate a_3 for the real wavefunction in Example 12.10.

12.22. For a true polyene (that is, an organic molecule having multiple conjugated carbon-carbon double bonds), there may be a small potential energy change on the ends that can be approximated by $V = k(x - a/4)^4$ where k is some constant. Apply this perturbation to the ground-state particle-in-a-box and determine its energy. You will have to multiply the function out into a polynomial and evaluate each term individually.

12.23. The Stark effect is the change in energy of a system due to the presence of an electric field (discovered by German physicist Johannes Stark in 1913). Consider the hydrogen atom. Its normally spherical 1*s* orbital distorts slightly when exposed to an electric field. If the electric field is considered to be in the z direction, then the field acts to introduce, or *mix,* some $2p_z$ character in with the 1*s* orbital. The atom is said to be *polarizable,* and the extent to which it changes is considered a measure of the atom's *polarizability* (which is designated by the letter α, not to be confused with the spin function α!). The perturbation Hamiltonian is defined as $\widehat{H}' = e \cdot E \cdot r \cdot \cos \theta$, where e is the charge on the electron, E is the strength of the electric field, and r and θ represent coordinates of the electron. Evaluate the perturbation energy of the hydrogen atom. You will have to integrate all three spherical polar coordinates in your evaluation of $\widehat{H}'$. (A similar effect, the *Zeeman effect,* exists for magnetic fields. It too can be treated using perturbation theory.)

12.7 & 12.8 Variation Theory

12.24. Which of the following unnormalized functions can be used in a variation theory treatment of a particle-in-a-box having length a?

(a) $\phi = \cos(Ax + B)$, A and B are constants

(b) $\phi = e^{-ar}$ **(c)** $\phi = e^{-ar^3}$

(d) $\phi = x^2(x - a)^2$ **(e)** $\phi = (x - a)^2$

(f) $\phi = a/(a - x)$ **(g)** $\phi = \sin(Ax/a)\cos(Ax/a)$

12.25. Confirm equation 12.29 by substituting the definitions in equation 12.28 into equation 12.27.

12.26. Show that a variation theory treatment of H using $\phi = e^{-kr}$ as an unnormalized trial function yields the correct minimum-energy solution for the hydrogen atom when the specific expression for k is determined.

12.27. Explain why assuming an "effective nuclear charge," as used for our treatment of the helium atom in Example 12.11, is unnecessary for a treatment of the hydrogen atom.

12.28. Show that the two real wavefunctions determined in Example 12.12 are orthonormal.

12.29. Consider a real system. Assume that a real wavefunction is a combination of two orthogonal functions such that $H_{11} = -15$, $H_{22} = -4$, and $H_{12} = H_{21} = -2.5$ (arbitrary energy units). **(a)** Evaluate the approximate energies of the real system and evaluate the coefficients of the expansion $\phi_a = c_{a,1}\Psi_1 + c_{a,2}\Psi_2$. **(b)** Compare your answer to the answers in exercise 12.12 and comment.

12.30. **(a)** What does the secular determinant look like for a system that is described in terms of four ideal wavefunctions? **(b)** Comment on the complexity of a secular determinant as the number of ideal wavefunctions increases. How many H and S integrals need to be evaluated?

12.31. Prove the variation theorem. Assume that the lowest possible energy of a system is E_1. Then, assume that any trial wavefunction ϕ can be written as a sum of the true wavefunctions Ψ_i of the system:

$$\phi = \sum_i c_i\Psi_i \qquad \text{where } \widehat{H}\Psi_i = E_i\Psi_i$$

Determine $\langle E \rangle$ using ϕ as the trial wavefunction and show that $\langle E \rangle \geq E_1$, equaling E_1 if ϕ is identically equal to Ψ_1 and greater than E_1 if ϕ is not identically equal to Ψ_1.

12.9 Comparing Variation and Perturbation Theories

12.32. In introducing both the variation and the perturbation theories, examples were given that had calculable answers, leaving the impression that the systems under consideration have ideal solutions. However, in all cases approximations were made. Identify the point in each theory introduction where an approximation is made that ultimately leads to an approximate, not exact, solution.

12.10 & 12.11 Born-Oppenheimer Approximation; LCAO-MO Theory

12.33. State the Born-Oppenheimer approximation in words and mathematically, and indicate how the mathematical form is implied by the statement.

12.34. Consider the diatomic molecules H_2 and Cs_2. For which is the Born-Oppenheimer approximation likely to introduce less error, and why?

12.35. Spectroscopy deals with differences in energy between levels. Derive an expression for ΔE, the difference in energy, between the two molecular orbitals of H_2^+.

12.36. Repeat the determination of $\phi_{H_2^+,1}$ and $\phi_{H_2^+,2}$ as well as E_1 and E_2 for R = 1.00, 1.15, 1.45, and 1.60 Å. Combine these with the determinations from Example 12.14 and construct a simple potential energy diagram for this system.

12.37. What is the bond order for the lowest excited state of H_2^+? From this single result, propose a general statement about *unstable* diatomic molecules and bond orders.

12.38. The helium atom was defined as two electrons and a single nucleus, and the hydrogen molecule ion was defined as a single electron and two nuclei. It seems that the only difference is an exchange in the identity of the particles in the system; however, their quantum mechanical treatment is completely different, as are the results. Explain why.

12.12 & 12.13 Molecular Orbitals; More Diatomic Molecules

12.39. Explain how we know that the first ϕ in equation 12.43 is the wavefunction for the bonding orbital, and that the second ϕ in equation 12.43 is the wavefunction for the antibonding orbital.

12.40. From Figure 12.23, give molecular electronic configurations for all diatomic molecules shown.

12.41. Use Figure 12.23 to determine electron configurations for O_2^{2+}, O_2^{-}, and O_2^{2-}.

12.42. Use molecular orbital arguments to decide whether or not the difluoride dianion, F_2^{2-}, should exist as a stable ion.

12.43. What is the bond order for the NO molecule? Use Figure 12.24 to determine an answer.

Symbolic Math Exercises

12.44. Use a math software program to determine the symbolic determinant of the 4 × 4 determinantal wavefunction for a Be atom, which has four electrons. Can you write the wavefunctions represented by the individual terms and identify the quantum numbers for each function?

12.45. Numerically evaluate the integral in Example 12.8 for $\langle E^{(1)} \rangle$ and demonstrate how much agreement there is to the given value of the energy correction of 5.450×10^{-18} J.

12.46. Use a symbolic math program to evaluate the trial wavefunction given in Example 12.11. Do you get the same value for Z'?

12.47. Evaluate the energies of the wavefunctions that are linear combinations of three terms whose energy and overlap integrals have the following values (in arbitrary units):

$H_{11} = 18$ $S_{11} = 0.55$

$H_{22} = 14$ $S_{22} = 0.29$

$H_{33} = 13.5$ $S_{33} = 0.067$

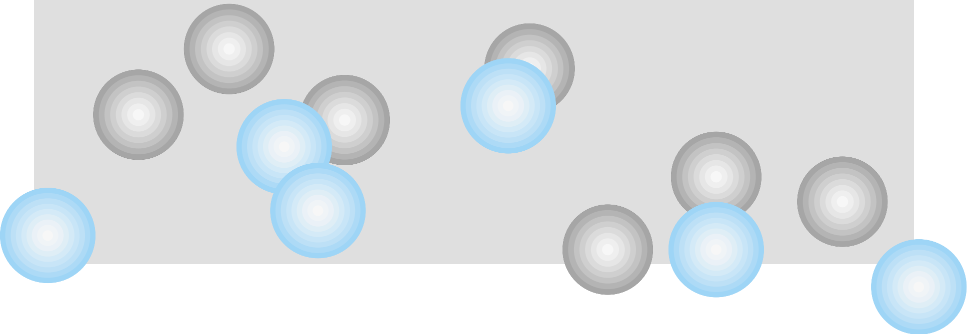
$H_{12} = 2.44$ $S_{12} = 0.029$

$H_{13} = 1.04$ $S_{13} = 0.006$

$H_{23} = 0.271$ $S_{23} = 0.077$

12.48. Evaluate equations 12.46 and 12.47 versus R, as R varies from 0 to 5 Å. Determine the value of R that minimizes the energy. What is the value of the energy at this minimum-energy distance?

13 Introduction to Symmetry in Quantum Mechanics



SYMMETRY IS ONE OF THE MOST POWERFUL TOOLS that can be applied to quantum mechanics and wavefunctions. Most people are generally aware of the concept of symmetry: an object is round or square, or the left side is the same as the right side, or maybe they are mirror images. All of these statements imply a recognition of symmetry, a spatial similarity due to the shape of an object. But more technically, symmetry is a powerful mathematical tool that can potentially simplify our study of quantum mechanics.

Consider a random quadrilateral, a plane figure having four sides. In order to define a specific quadrilateral, one must specify not only the lengths of each side, but their order and angles of intersection. Now consider a square. A square is also a plane figure having four sides. But by definition, the sides are at 90° angles and all have the same length. A square has more *symmetry,* and so is simpler to define.

Such comparisons apply in quantum mechanics, too. Recognizing the symmetry of an atomic or molecular system allows one to simplify the quantum mechanics, sometimes dramatically. We have already seen some aspects of symmetry: odd and even functions, the spherical nature of the hydrogen atom's 1*s* orbital, the cylindrical shape of H_2^+ and H_2. All these are applications of symmetry. In this chapter, we will develop a general understanding of symmetry using a mathematical tool called group theory. Then, we can see how symmetry applies to some aspects of quantum mechanics.

13.1 Synopsis

This chapter begins with an introduction to group theory, the branch of mathematics that considers symmetry. We will find that each symmetry operation has a corresponding symmetry operator, just like other quantum-mechanical operators. Symmetry operators move objects, including molecules, in three-dimensional space into spatially equivalent objects. Every object satisfies a collection, or *group,* of symmetry operators. Understanding the characteristics of that group of operators is an important part of symmetry. At first, there will be little connection between symmetry and the topics of the previous chapters, but that will change quickly. Wavefunctions also have symmetry, and their symmetry can be used to understand their properties and to define and describe molecular wavefunctions more easily (like the example of the quadrilateral and square above). Symmetry considerations are important in approximating molecular orbitals as linear combinations of atomic orbitals. Finally, we will consider the shapes of molecules, how their shapes are dictated by the atomic orbitals of the atoms, and how such orbitals can be better described as combinations called hybrid orbitals. Symmetry is also applicable to such hybrid orbitals in a natural way.

13.2 Symmetry Operations and Point Groups

Consider the rectangle in Figure 13.1. When you rotate the rectangle by 180° or π radians, the resulting figure looks identical to the original. Imagine an axis through the center of the rectangle and the shape rotating about that axis by 180°. Such an axis is called an *axis of symmetry.* A shape like a rectangle has several axes of symmetry; for each one the rotation occurs about a different spatial axis. The rotation of the rectangle to generate an equivalent rectangle is an example of a *symmetry operation.* A symmetry operation is any movement of an object that leaves the object looking as it did originally. The axis about which the rotation occurs is an example of a *symmetry element.* A symmetry element is a point, line, or plane (or combination thereof).

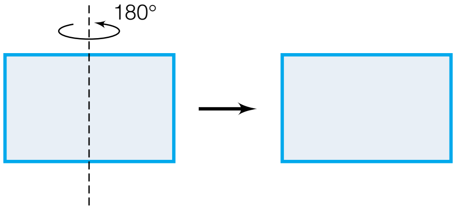


Figure 13.1 A rectangle is a simple example of an object that has symmetry. For example, rotating the rectangle 180°, an operation labeled C_2, produces a rectangle that is indistinguishable from the original object. Can you find two other axes of rotation for this rectangle?

Rotations are not the only simple symmetry operation. Imagine a plane at right angles to the rectangle, cutting it in half, as shown in Figure 13.2. Reflect every point on the rectangle through the plane, as if it were a mirror. The original shape is present after the reflection. Such a symmetry operation is called a *reflection plane of symmetry.* In this case, the plane is the symmetry element through which reflection occurs.

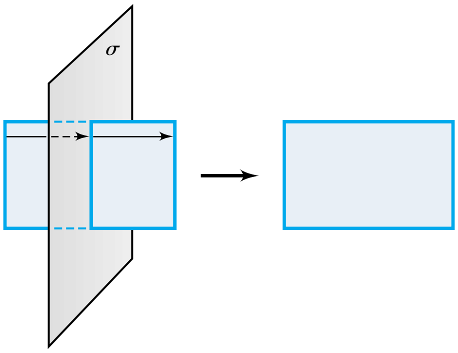


Figure 13.2 A rectangle has reflection planes of symmetry, labeled σ. Upon reflection of all points of the rectangle through the plane of symmetry, the original object is reproduced. The reflection of only one point on the rectangle is shown. Can you find two other reflection planes of symmetry for the rectangle?

Consider the point at the center of the rectangle, Figure 13.3. Take every point on the rectangle and pass it through the center and place it on the opposite side of the center, the same distance away. The resulting rectangle looks the same as it did originally. This symmetry operation is called *inversion,* and a *center of inversion* is the corresponding symmetry element.

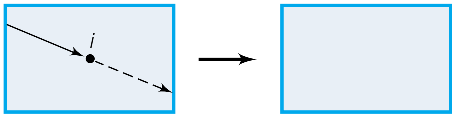


Figure 13.3 A rectangle has a center of inversion, labeled i. Reflection of every point of the rectangle through the center of inversion produces a rectangle that is indistinguishable from the original object. Reflection of only one point on the rectangle is shown. An object can have only one center of inversion.

The three examples above represent general types of symmetry operations. Each general type of symmetry operation is given a symbol to represent it. An axis of symmetry is denoted C_n, where n is the number of times the operation has to be repeated in order for the object to return to its *original* starting position. It can be shown that $n = 360°/\theta$, where θ is the angle of rotation needed for the object to look like it originally did. The axis for the rectangle above is a C_2 axis. Planes of symmetry are given the symbol σ, and the center of inversion is indicated by i. (This should not be confused with i, the square root of -1.)

There are two other types of symmetry operations. The first is called the *identity element,* represented by E. Everything has E as a symmetry operation; it is the symmetry operation due to the object's very existence. The last symmetry operation is an *improper axis of symmetry,* indicated by S_n. (C_n is more specifically called a *proper rotation.*) It is a combination of a C_n rotation (that is, turning on an axis by $360°/n$) followed by reflection through a plane that is perpendicular to the axis. Figure 13.4 illustrates the S_n symmetry operation. S_1 is equivalent to a σ symmetry operation, and S_2 is equivalent to a center of inversion, i. The rotational part of the S_n symmetry element may or may not correspond with an existing axis of symmetry.

Molecules also possess symmetry elements. Depending on the identities and positions of atoms in a molecule, any molecule will have certain symmetry

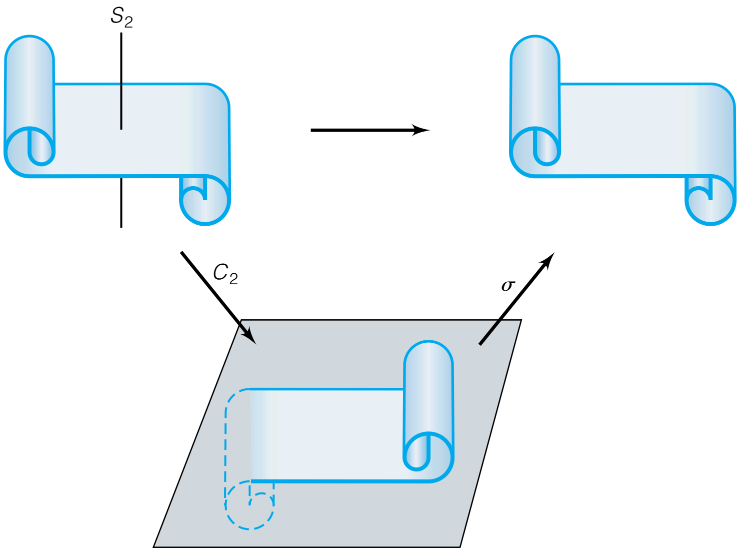


Figure 13.4 The scroll pictured has an S_2 symmetry element. It is the combination of a C_2 rotation and a reflection through a plane that is perpendicular to the C_2 axis. The C_2 operation switches the curls on the scroll, and the resulting reflection returns the curls' positions back to their original orientation. The improper axis of rotation does this as a single symmetry element. Note that although the scroll has an S_2 symmetry element, neither the C_2 axis nor a σ plane as indicated are, by themselves, symmetry elements of the object.

elements such that operation on that molecule by the corresponding symmetry operations will produce a "new" orientation in space that is indistinguishable from the original orientation. Figure 13.5 shows the symmetry elements for a simple molecule, H_2O. The ability to recognize symmetry elements in a molecule will be an important skill to develop.

Real objects, including molecules, do not have any random set of symmetry elements. Only certain specific *groups* of symmetry elements are possible for any physical object. Because all of the symmetry elements of such a group intersect at a single point in the object, such groups are called *point groups.* A point group is usually referred to by a label to indicate that an object contains that certain set of symmetry elements. For example, the C_{2v} point group, which describes the symmetry of the water molecule, consists of E, a C_2 proper rotation, and two planes of symmetry σ. Consider the symmetry elements for H_2O in Figure 13.5. All objects that have C_{2v} symmetry contain *these four and no other* symmetry elements. Examples of point groups and their symmetry elements are listed in the Appendix 3 character tables. The tabulations of point groups in Appendix 3 contain additional information whose utility will become clearer in the next few sections. For now, you should learn to identify all the symmetry elements of any given point group.

A real object can possess more than one of the same type of symmetry element. For example, benzene has several rotational axes, as shown in Figure 13.6a. In real objects, the proper axis of rotation that has the largest n (an n-fold axis) is called the *principal axis.* It is conventional to consider the principal axis to be the z-axis in 3-D space. In the identification of axes of rotation, both directions of rotation (clockwise and counterclockwise) need to be considered independently, so that a rotation of 90° in a clockwise direction is not the same as a 90° rotation in the counterclockwise direction.

Finally, there are different types of planes of symmetry. For example, in the rectangle are three different planes of symmetry, including the plane that the

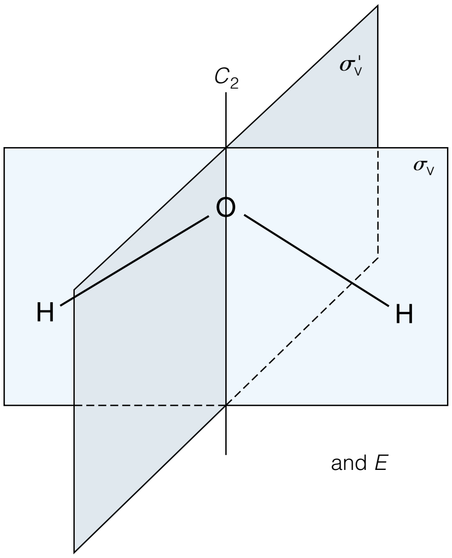


Figure 13.5 The four symmetry operations present in H_2O. The molecule has the E symmetry element by virtue of its existence. Collectively, these four symmetry operations define the C_{2v} point group.

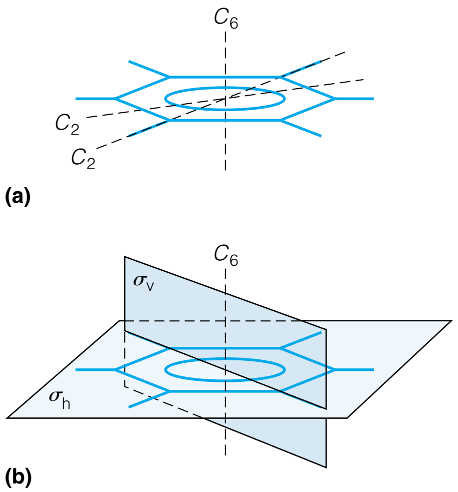


Figure 13.6 (a) The benzene molecule has one sixfold principal axis of symmetry, C_6. It also has several C_2 axes of symmetry perpendicular to the principal axis, in the plane of the molecule. Only two are shown. Can you find all of the other axes of symmetry? (b) Reflection planes are *vertical* planes if they contain the principal axis of symmetry, and *horizontal* planes if they are perpendicular to the principal axis. There are also *dihedral* planes, which are vertical planes that bisect two intersecting C_2 axes of symmetry. In the benzene molecule, the vertical planes are actually dihedral planes.

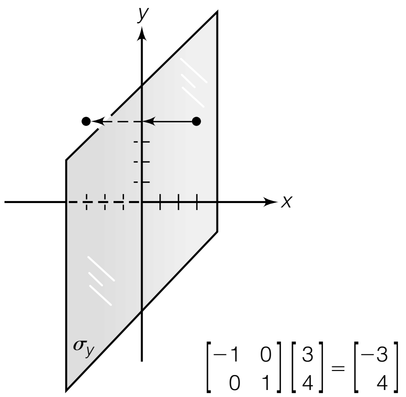


Figure 13.7 Symmetry operations can also be defined mathematically. Here, the reflection of the point (3, 4) through the y-axis is equivalent to the product of two matrices, one representing the point and one representing the symmetry operation.

rectangle is lying in. In real objects, planes that contain the principal axis are considered *vertical planes* of symmetry and are given the symbol σ_v. Planes of symmetry that are perpendicular to the principal axis are called *horizontal planes* and are symbolized σ_h. If a vertical plane lies exactly in the middle between two C_2 axes that are perpendicular to the principal axis, it is called a *dihedral plane* and is given the symbol σ_d. (The presence of dihedral planes implies a "higher" symmetry than regular vertical planes.) Figure 13.6b shows some of the different types of planes in the benzene molecule; not all of the planes of symmetry are shown, for the sake of clarity. In order to standardize the labeling of multiple symmetry elements of the same kind in highly symmetric systems, different axes and planes are sometimes differentiated with single and multiple primes.

It is easy to think of symmetry operations as spatial motions of objects that reproduce the original object. However, symmetry operations can be defined mathematically. Consider the point (3, 4) in 2-D Cartesian coordinates shown in Figure 13.7. Reflection through the y-axis moves this point to (−3, 4). The x coordinate has changed sign, as shown in Figure 13.7. Although we can conclude that reflection through the y-axis, labeled σ_y, acts to change the sign of the x coordinate, we need a more general mathematical definition of σ_y. Matrix algebra is useful for this. A simple diagonal matrix is used to define the symmetry operation so that the multiplication of the symmetry operation and the original coordinates generates the new coordinates. In this case, we would have

$$\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 3 \\ 4 \end{bmatrix} = \begin{bmatrix} -3 \\ 4 \end{bmatrix}$$

where the coordinates are written in columns ("column matrices" or "column vectors"). Standard matrix multiplication generates the new coordinates. This implies that the particular symmetry operation σ_y is defined as

$$\sigma_y = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \tag{13.1}$$

and that this symmetry operation is operating on the original coordinates to generate new coordinates. That is, symmetry operations act as mathematical *operators*. In general, the performance of any symmetry operation on a point can be represented as the matrix multiplication of the symmetry operation (written in square-matrix form) on that point (written in column vector form).

This example considers a single point on a graph. Now consider our rectangle, superimposed about the origin in two-dimensional Cartesian space. Operate on *every point* of the rectangle with σ_y and consider the new shape. It is the same as the original shape, as shown in Figure 13.8. Therefore we can say that the rectangle has the symmetry element σ_y, whose operation is defined by the above two-dimensional expression.

For real systems, three-dimensional space is considered. All symmetry operations can be defined by a specific 3 × 3 matrix. As such, all symmetry operations can act as operators on a set of points to generate a new set of points. If the new set of points is in exactly the same position as the original, then that set of points is said to contain the corresponding symmetry element. Table 13.1 lists the matrices that define the symmetry operations. In molecules, the atomic positions will represent our points in three-dimensional space. Instead of using a 3 × 3 matrix to describe the symmetry operation, each atom will require a 3 × 3 "block" of a larger matrix to describe its change in position in space

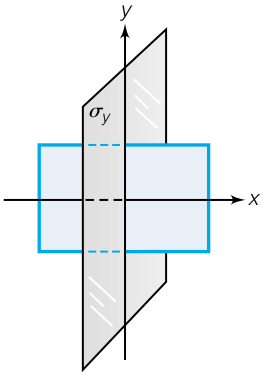


Figure 13.8 The rectangle's symmetry operations can also be defined mathematically. In this case, the symmetry operation σ operates on the rectangle to produced an equivalent rectangle.

Table 13.1 General matrix representations of the five types of symmetry operations[a]

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad C_n = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad \theta = \frac{360°}{n}$$

$$\sigma_z = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$S_n = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}, \quad \theta = \frac{360°}{n}$$

[a] Matrices are in 3 × 3 form. The rotations are assumed to occur about the *z*-axis, and the plane is assumed to be the *xy* plane so that only the *z* coordinate is affected.

due to the symmetry operation. For a molecule having N atoms, this will require a $3N \times 3N$ matrix—but there are some major simplifications, as we shall see.

Example 13.1

Show how the equation $y = x$ has a center of inversion at $x = 0$.

Solution

From Table 13.1, the complete matrix definition of i is

$$i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Consider any point in the upper right (x, y) quadrant of a standard 2-D graph. The value of z in this case is zero, so the 3-D coordinate set is $(x, y, 0)$. Operating on this point with the inversion symmetry operation:

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ 0 \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ 0 \end{bmatrix}$$

Is the point $(-x, -y, 0)$ a point on the line $y = x$? Yes, it is, for any value of x. Such points are in the lower left quadrant. Therefore, this equation contains a center of inversion. To convince yourself of this, plot the graph and repeat the example.

13.3 The Mathematical Basis of Groups

We have established two things about symmetry operations. First, they are operators and expressed mathematically in terms of a 3 × 3 matrix for operations on a point in 3-D space. Second, we have stated that only certain collections of symmetry elements, called point groups, are possible for real objects.

The area of mathematics that deals with symmetry and point groups is called *group theory*. A *group* is a certain collection of operations that satisfies the following conditions:

- The group must have an *identity operation* such that operation by identity does not change the object. This operation must be commutative

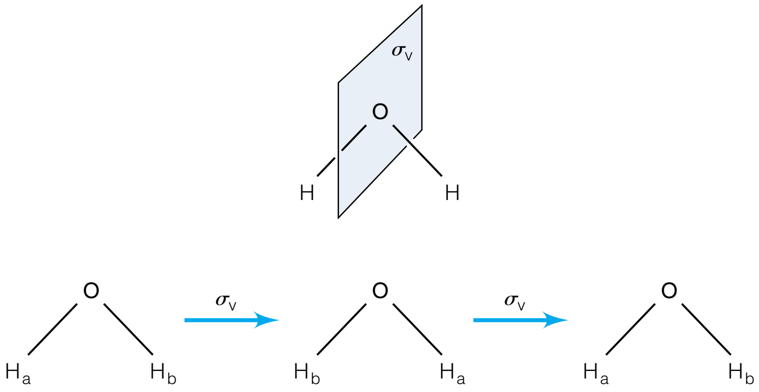


Figure 13.9 The symmetry operation σ_v is its own inverse.

with all other operations of the group. That is, if A represents the identity operation and B represents any other operation, then the combination AB has the same effect as the combination BA which has the same effect of the B operation by itself.

- An *inverse operation* must be present for every operation in the point group that reverses the action of each operation. Some operations are their own inverse.
- In combinations of more than one operation, the *associative law* applies. This means that if you have three symmetry operations labeled A, B, and C, the combinations $(AB)C$ and $A(BC)$ must yield the same overall effect.
- Every possible combination of more than one operation in the group must be equivalent to a single operation of the group. This property is called *closure.*

We have already defined the identity operation E, which is a member of all point groups. Consider the inverse operation requirement. Assume that one can keep track of the individual identity of the hydrogens in the water molecule shown in Figure 13.9. Operation on the molecule by the σ_v shown switches the positions of the hydrogens. A second operation on the molecule moves the hydrogens back to their original positions. This shows that the σ_v is its own inverse. All planes of symmetry are their own inverse.

Application of C_2 to the water molecule also returns the atoms to their original starting points, so C_2 is also its own inverse. However, consider NH_3 (Figure 13.10). It has a threefold axis C_3 passing through the N, but application of the C_3 operation does not return the atoms to their original positions, as shown. There are two choices. Either the molecule can be rotated by 120° in the opposite direction, which would be labeled C_3^{-1}. Or, the molecule can be rotated by 240°, or two-thirds of a complete circle, which would return the atoms to their original points. This operation would be labeled C_3^2. Each operation is equivalent. It is customary to consider that all rotations about the same axis are performed in the same direction, so the operation of choice would be C_3^2. What this means is that the NH_3 molecule has just one threefold *axis,* but two different rotational symmetry *operations* about that axis. Both symmetry operations must be defined in order for the symmetry operations to constitute a mathematical group.

The association requirement and the closure requirement both refer to situations in which more than one symmetry operation is performed sequen-

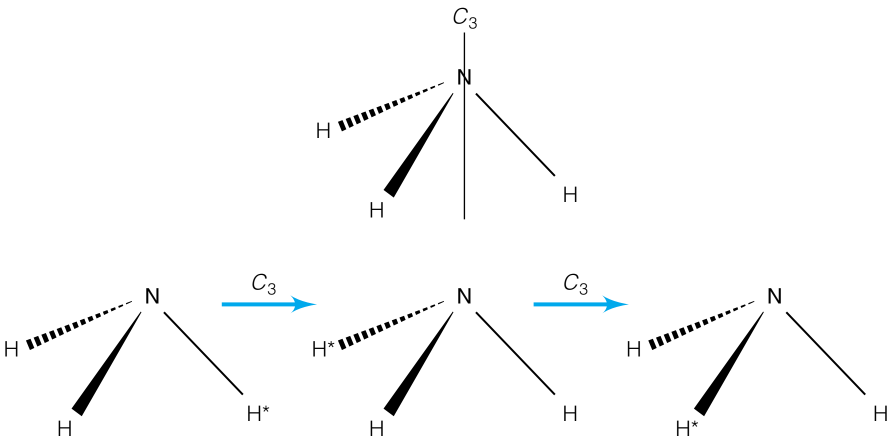


Figure 13.10 C_3 is not its own inverse. The ammonia molecule needs another symmetry operation to rotate to its original position.

tially. For our purposes, the closure requirement is more important. Any combination of symmetry operations in a point group is equivalent to a *single* operation of that group. Again, consider the molecule NH_3, which has the point group C_{3v}. It consists of E, C_3, C_3^2, σ_v, σ_v', and σ_v''. The corresponding symmetry elements are illustrated in Figure 13.11. What is the consequence of operating an NH_3 molecule with C_3 and then σ_v? Figure 13.12 shows these two operations with the hydrogens labeled so we can keep track of their relative positions. Figure 13.12 also shows that performing a single operation, σ_v'', will exchange the atoms in NH_3 in the same way that the combination of C_3 and σ_v did. This is an example of the closure requirement for groups. All combinations of symmetry operations in a group behave similarly.

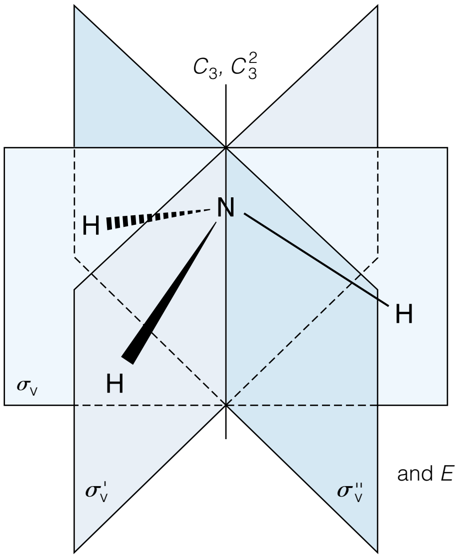


Figure 13.11 The six symmetry operations of ammonia, NH_3. One N–H bond lies in each plane of symmetry. Collectively, these six symmetry operations compose the C_{3v} point group.

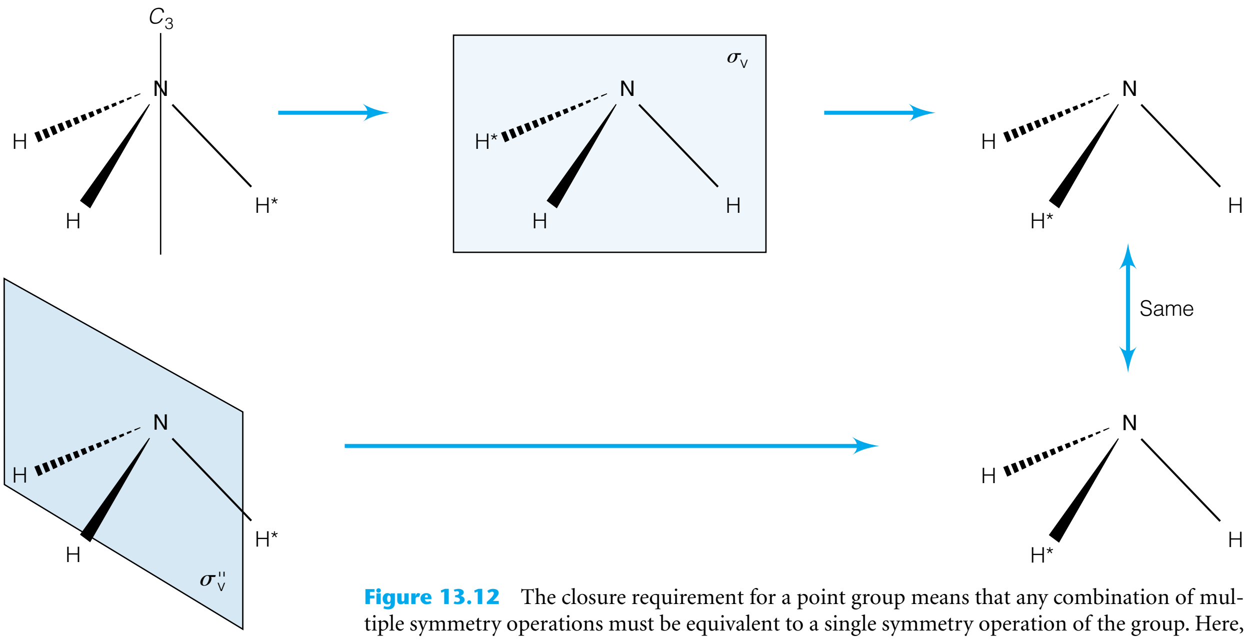
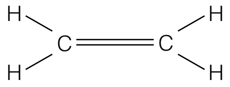


Figure 13.12 The closure requirement for a point group means that any combination of multiple symmetry operations must be equivalent to a single symmetry operation of the group. Here, the two symmetry operations C_3 and σ_v are shown to be equivalent to the σ''_v operation of the C_{3v} point group.

Example 13.2

Identify the symmetry elements in ethylene, which has the structure



From the tables in Appendix 3, determine its point group.

Solution

Ethylene has E, three independent C_2 axes, three independent planes of symmetry, and a center of inversion. This total of eight symmetry elements composes the D_{2h} point group.

The number of individual symmetry operations in a point group is called the *order* of the group and is symbolized by the letter h (not to be confused with Planck's constant). In the above example, the D_{2h} point group has an order of 8. Symmetry operations in a point group are occasionally grouped together for reasons we will see later. For example, the C_{3v} point group treats C_3 and C_3^2 together, as well as the three planes of symmetry. As such, it is common to see that the symmetry operations of the C_{3v} point group are listed as E, $2C_3$, and $3\sigma_v$. Each collection of one or more symmetry operations is called a *class*. E is always in its own class. Only similar symmetry operations are grouped together in classes, but not all of the same symmetry operations can be grouped together in the same class. For example, the C_{2v} point group lists σ_v and σ'_v separately, indicating that they are not grouped together in the same class. One can say that the C_{3v} point group has three classes and an order of 6, and the C_{2v} point group has four classes and $h = 4$.

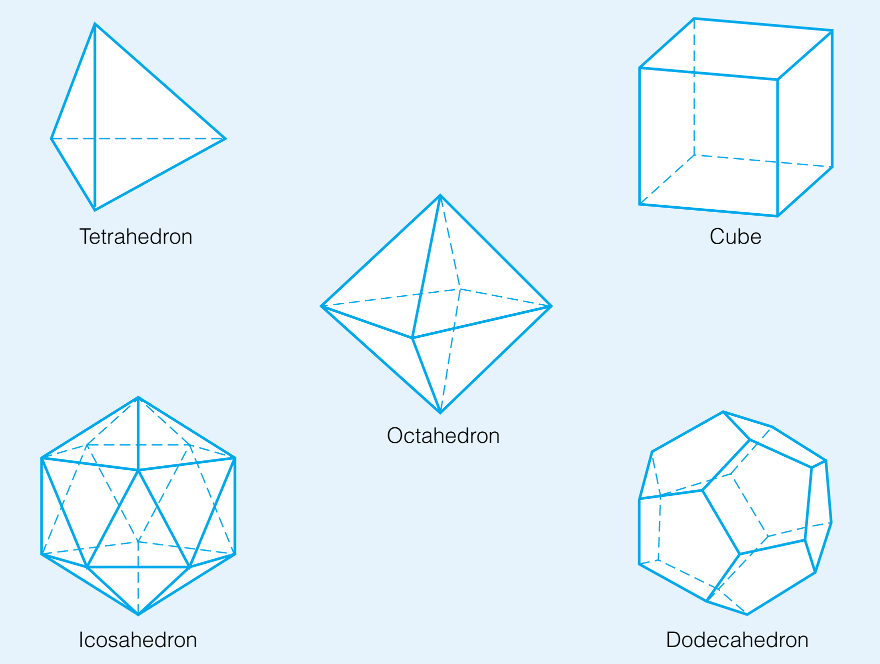


Figure 13.13 The five Platonic solids—tetrahedron, cube, octahedron, dodecahedron, and icosahedron. Collectively, these five shapes represent the cubic point groups.

Finally, some point groups have certain interesting symmetry elements. Any linear system possesses a C_∞ axis along the system axis. Therefore, there are $C_{\infty v}$ and $D_{\infty h}$ point groups that have this element. Some systems have a large number of symmetry elements that include several highfold principal axes. Such point groups are called *cubic groups* and consist of tetrahedral, octahedral, and similarly named groups. All five of the Platonic solids (tetrahedron, cube, octahedron, dodecahedron, and icosahedron, as shown in Figure 13.13) have cubic symmetry. Finally, there is the symmetry group that defines a sphere, which contains E, arbitrary C_∞ and S_∞ axes, and a center of inversion. This group is labeled $R_h(3)$ and is called the three-dimensional full rotation group. It has particular application for atomic wavefunctions, since individual atoms can be treated as if they were perfect spheres (which take on nonspherical symmetry only when some other influence is imposed: bonding to other atoms or being surrounded by ions in a crystal, for example). For real objects, only a finite number of point groups are possible.

13.4 Molecules and Symmetry

All molecules have a structure belonging to one of the recognized point groups. Although we have used molecules as examples of systems that have symmetry elements, we have only assumed this idea so far. Most molecules actually possess very few symmetry elements, and so can be spoken of as having "low" symmetry. All of them have at least E, and so can be recognized as having an overall symmetry defined at least by the point group C_1. Many molecules, especially smaller ones, have more symmetry elements and so are said to have "higher" symmetry. For example, the molecule CH_4 has the shape of a tetrahedron, which has a very high cubic symmetry. Whatever the molecule, its structure can be assigned to a point group on the basis of its symmetry

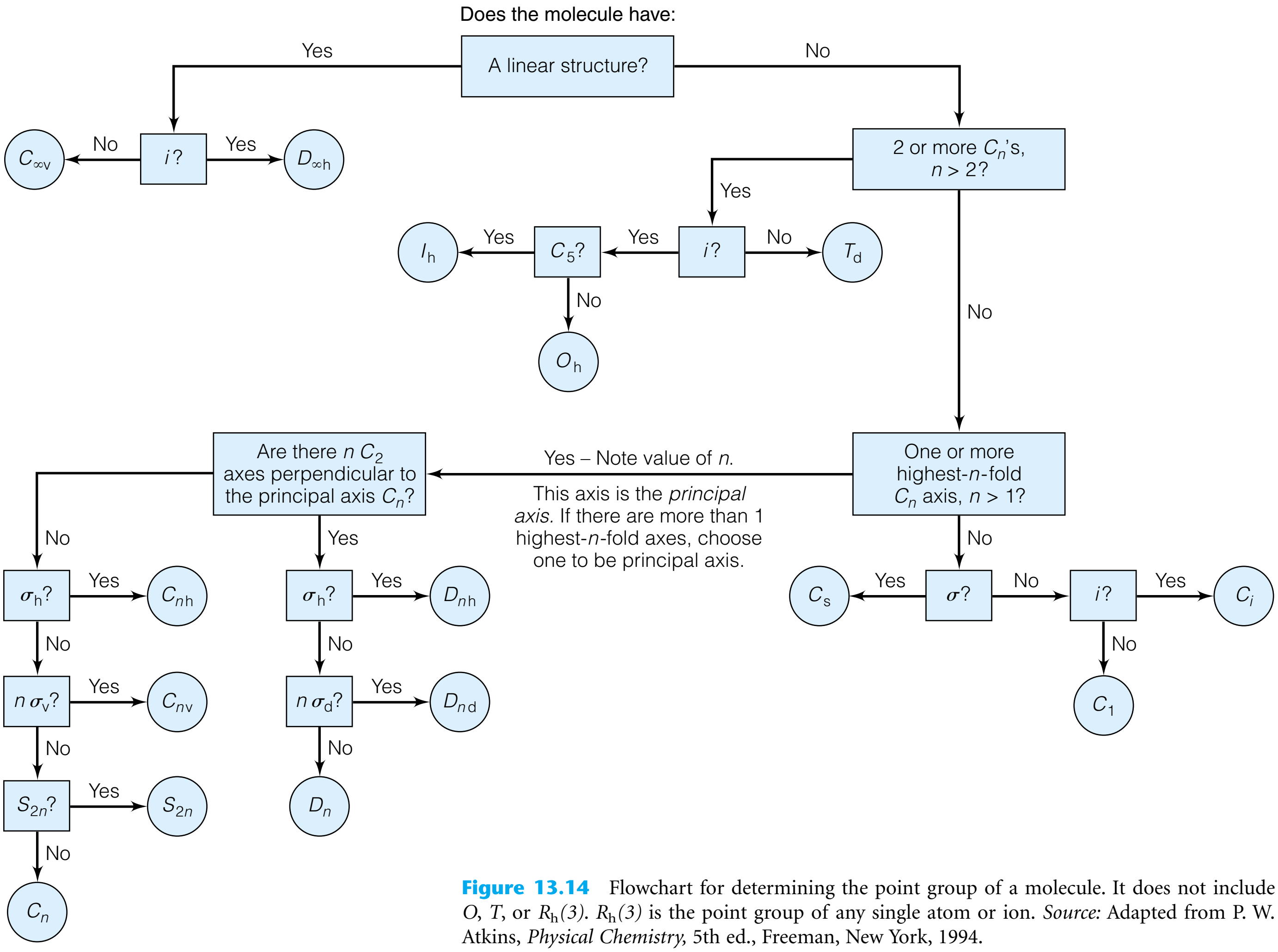


Figure 13.14 Flowchart for determining the point group of a molecule. It does not include *O*, *T*, or $R_h(3)$. $R_h(3)$ is the point group of any single atom or ion. *Source:* Adapted from P. W. Atkins, *Physical Chemistry,* 5th ed., Freeman, New York, 1994.

elements. One can either determine all of the symmetry elements of a given molecule and compare it to the (relatively short) list of point groups, or one can use a flowchart like the one reproduced in Figure 13.14.

Example 13.3

Determine the point groups that define the symmetry of the following compounds, whose structures are illustrated in Figure 13.15.

a. Hydrogen sulfide, H_2S
b. Sulfur hexafluoride, SF_6
c. Acetylene, C_2H_2
d. Benzene, C_6H_6
e. The nitrate ion, NO_3^- (assume resonance averages the structure into a flat, triangular species).

Solution

Using Figure 13.14, satisfy yourself that the following point groups are indeed correct by identifying the individual symmetry elements, if any exist other than *E*.

a. H_2S: C_{2v}, just like H_2O.

b. SF_6: O_h. This molecule has the shape of an octahedron.

c. C_2H_2: $D_{\infty h}$, since it is linear and symmetric (if it had no center of inversion, it would be $C_{\infty v}$).

d. C_6H_6: D_{6h}.

e. NO_3^-: D_{3h}.

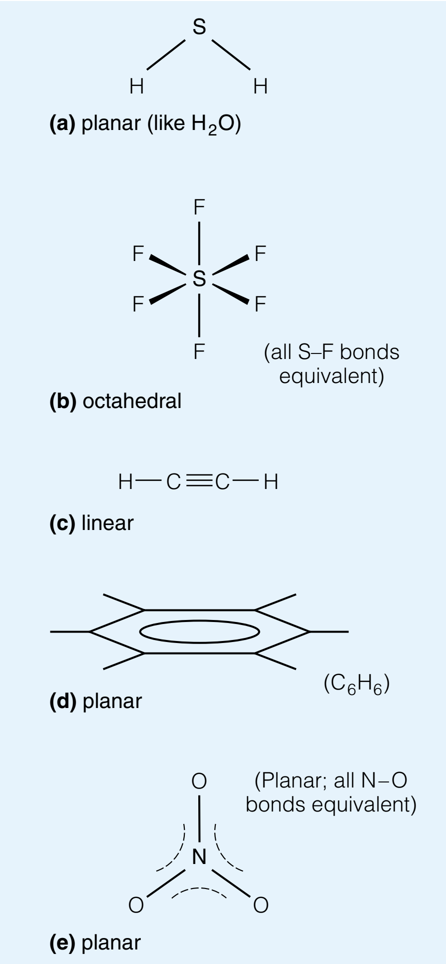


Figure 13.15 What are the point groups of these five molecules? See Example 13.3.

The applicability of symmetry to molecules is deeper than just the shape of the molecule. Mathematical equations also have symmetry properties. We have already discussed the concept of odd and even functions. This is a symmetry property. An even function implies that a plane of symmetry exists, typically a plane that intersects the y-axis. You can verify this by looking at plots of cosine, an even function, and sine, an odd function.

As mathematical functions, quantum-mechanical wavefunctions can also have certain symmetry properties. But what symmetry properties does a wavefunction have? Since a wavefunction determines the distribution of electron probability in a molecule, and that distribution of electrons ultimately gives a molecule its shape, we conclude that the wavefunction of a molecule must possess the same symmetry elements as the molecule itself. Thus, if the symmetry elements of a molecule are identified, then the wavefunctions of the molecule should have the same symmetry elements, and belong to the same point group, as the molecule. It is this idea that makes symmetry a valuable tool in quantum mechanics.

Example 13.4

a. What is the point group of the wavefunction for the $1s$ orbital of H?

b. What is the point group of the wavefunction for the $2p_z$ orbital of H? (See Figure 13.16.)

Solution

a. The $1s$ wavefunction is spherically symmetric, having E, i, and an infinite number of C_ϕ and S_ϕ and σ symmetry elements. (The ϕ subscript on the C and S means that the rotation can be any angle and still be a symmetry operation.) It would belong to the special point group $R_h(3)$.

b. The $2p_z$ wavefunction is not spherically symmetric by itself, but it does have the symmetry elements E, infinite σ_v's, and C_∞. Because of the difference in sign of the wavefunction on either side of the nodal plane, it does not have a center of inversion (despite appearances). Therefore it belongs to the $C_{\infty v}$ point group. (This does not imply that the hydrogen atom itself has $C_{\infty v}$ symmetry; only this particular $2p_z$ atomic orbital.)

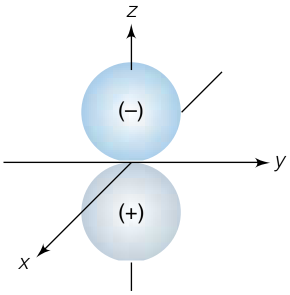


Figure 13.16 A $2p_z$ orbital of H. See Example 13.4b.

Example 13.5

Indicate what symmetries the wavefunctions of the following molecules must have.

a. Water, H_2O

b. Benzene, C_6H_6

c. Allene, $CH_2{=}C{=}CH_2$

d. Bromochlorofluoromethane, CHBrClF

Solution

Because wavefunctions for molecules must have the same symmetry as the molecule, one must identify the molecule's symmetries. Figure 13.14 can be used to determine the following point groups of the molecules and, therefore, their wavefunctions.

a. H_2O: C_{2v}
b. C_6H_6: D_{6h}
c. Allene: D_{2d}
d. CHBrClF: C_1

We will return to the application of symmetry to wavefunctions in a later section. Symmetry in molecules has several immediate consequences. For example, the dipole moment of a molecule depends in part on how the atoms in the molecule are arranged. It can be shown that any molecule whose structure has a point group symmetry of C_s, C_n, or C_{nv} , with $n > 1$, is polar, and molecules that do not have such symmetry are nonpolar. Further, it can also be shown that any molecule *may* be chiral if it does *not* contain an S_n $(n \geq 1)$ symmetry element. However, chirality is not guaranteed if the molecule does not possess an improper axis of symmetry (for example, H_2O does not have an improper rotation axis but is not chiral). Chirality is an important issue in organic chemistry and is the basis of stereochemistry.

13.5 Character Tables

Now that the importance of symmetry in wavefunctions has been established, some of the utility of symmetry can be introduced. A water molecule, H_2O, is in the position indicated by Figure 13.17. H_2O has all of the symmetry elements described by the C_{2v} point group, so it has E, C_2, and two σ_v's, which we will designate $\sigma(xz)$ and $\sigma(yz)$. Remembering from above that each symmetry operation can be defined as a matrix, we can construct matrices to define the symmetry operations for H_2O. However, *each atom* in the molecule has

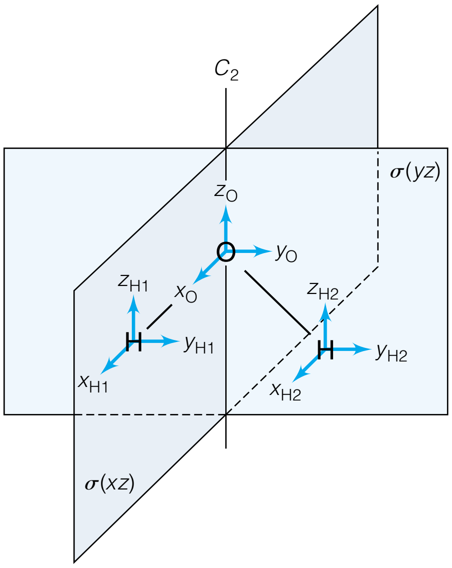


Figure 13.17 The H_2O molecule, the Cartesian degrees of freedom of the atoms, and the symmetry operations of the C_{2v} point group.

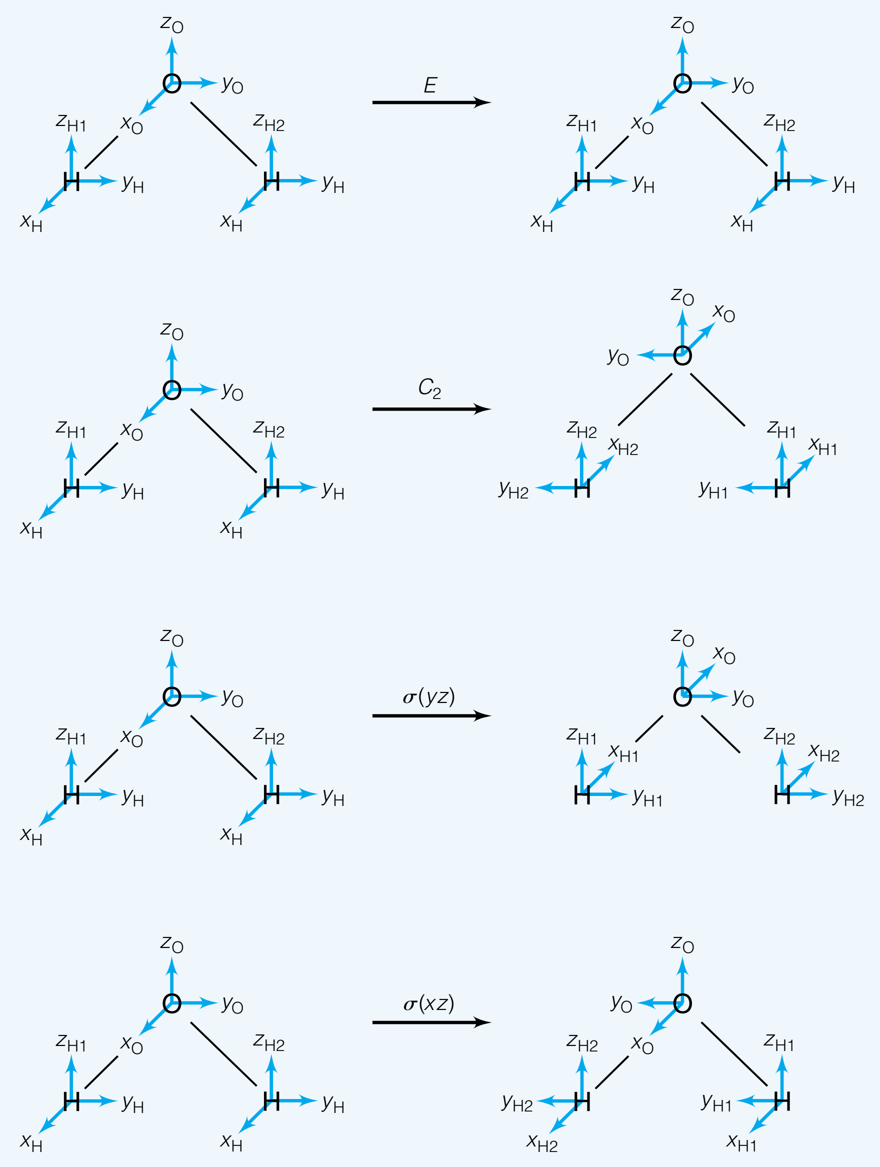


Figure 13.18 The effect of the four symmetry operations of C_{2v} on the degrees of freedom of the H_2O molecule. E does nothing. C_2 and $\sigma(xz)$ exchange the two hydrogens and reverse the directions of some of the coordinate unit vectors. $\sigma(yz)$ does not move any atoms but reverses some coordinate vectors. You should be able to reconcile the above diagrams with the matrices in equation 13.2.

x, y, and z coordinates, so there are a total of $3N$ (N = number of atoms) total coordinates for the molecule. Furthermore, one needs to keep track of the original positive directions of the x, y, and z axes, as shown in Figure 13.17. Instead of the 3 × 3 matrices defined above, we therefore have to construct a 9 × 9 matrix to describe the complete spatial effect of each symmetry operation, shown visually in Figure 13.18:

$$E(\mathrm{H_2O}) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_{\mathrm{H1}} \\ y_{\mathrm{H1}} \\ z_{\mathrm{H1}} \\ x_{\mathrm{O}} \\ y_{\mathrm{O}} \\ z_{\mathrm{O}} \\ x_{\mathrm{H2}} \\ y_{\mathrm{H2}} \\ z_{\mathrm{H2}} \end{bmatrix} = \begin{bmatrix} x_{\mathrm{H1}} \\ y_{\mathrm{H1}} \\ z_{\mathrm{H1}} \\ x_{\mathrm{O}} \\ y_{\mathrm{O}} \\ z_{\mathrm{O}} \\ x_{\mathrm{H2}} \\ y_{\mathrm{H2}} \\ z_{\mathrm{H2}} \end{bmatrix}$$

$$C_2(\mathrm{H_2O}) = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} x_{\mathrm{H1}} \\ y_{\mathrm{H1}} \\ z_{\mathrm{H1}} \\ x_{\mathrm{O}} \\ y_{\mathrm{O}} \\ z_{\mathrm{O}} \\ x_{\mathrm{H2}} \\ y_{\mathrm{H2}} \\ z_{\mathrm{H2}} \end{bmatrix} = \begin{bmatrix} -x_{\mathrm{H2}} \\ -y_{\mathrm{H2}} \\ z_{\mathrm{H2}} \\ -x_{\mathrm{O}} \\ -y_{\mathrm{O}} \\ z_{\mathrm{O}} \\ -x_{\mathrm{H1}} \\ -y_{\mathrm{H1}} \\ z_{\mathrm{H1}} \end{bmatrix} \tag{13.2}$$

$$\sigma(yz)(\mathrm{H_2O}) = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_{\mathrm{H1}} \\ y_{\mathrm{H1}} \\ z_{\mathrm{H1}} \\ x_{\mathrm{O}} \\ y_{\mathrm{O}} \\ z_{\mathrm{O}} \\ x_{\mathrm{H2}} \\ y_{\mathrm{H2}} \\ z_{\mathrm{H2}} \end{bmatrix} = \begin{bmatrix} -x_{\mathrm{H1}} \\ y_{\mathrm{H1}} \\ z_{\mathrm{H1}} \\ -x_{\mathrm{O}} \\ y_{\mathrm{O}} \\ z_{\mathrm{O}} \\ -x_{\mathrm{H2}} \\ y_{\mathrm{H2}} \\ z_{\mathrm{H2}} \end{bmatrix}$$

$$\sigma(xz)(\mathrm{H_2O}) = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} x_{\mathrm{H1}} \\ y_{\mathrm{H1}} \\ z_{\mathrm{H1}} \\ x_{\mathrm{O}} \\ y_{\mathrm{O}} \\ z_{\mathrm{O}} \\ x_{\mathrm{H2}} \\ y_{\mathrm{H2}} \\ z_{\mathrm{H2}} \end{bmatrix} = \begin{bmatrix} x_{\mathrm{H2}} \\ -y_{\mathrm{H2}} \\ z_{\mathrm{H2}} \\ x_{\mathrm{O}} \\ -y_{\mathrm{O}} \\ z_{\mathrm{O}} \\ x_{\mathrm{H1}} \\ -y_{\mathrm{H1}} \\ z_{\mathrm{H1}} \end{bmatrix}$$

Not only do the hydrogen atoms exchange places in $\sigma(xz)$ and C_2, but some of their unit vectors have also reversed direction. This accounts for the appearance of some negative signs in the product matrices. You should satisfy yourself that these matrices and the diagrams in Figure 13.18 do coincide with each other.

Each of the 9 × 9 matrices in equation 13.2 is called a *representation* of the corresponding symmetry operation. These representations are complete, but cumbersome. And this just for a molecule that has three atoms. For N atoms, the $3N \times 3N$ matrix contains $9N^2$ terms. Therefore the complete representation for dimethyl ether, $(\mathrm{CH_3})_2\mathrm{O}$, which also has C_{2v} symmetry, can be defined by four 27×27 matrices with each having $27^2 = 729$ numbers in it! To be sure, most of them are zero (as they are above), but determining which are exactly zero is a chore. Dimethyl ether is still a rather small molecule. We need a simpler representation.

The representations above can be dramatically simplified, so they are called *reducible representations.* Ultimately we are after the simplest possible representations of the symmetry operations of a point group, which are called the *irreducible representations.* The trick to defining such irreducible representations is to recognize the patterns in the 9 × 9 representations above. For example, in this case the symmetry operation E multiplies each coordinate by 1:

$$E(\text{coordinate}) = 1 \times (\text{coordinate}) \tag{13.3}$$

As such, why not simply use the number 1 to represent the effect of E on that coordinate?* In this case, that would work fine. However, for the other symmetry operations in the above example, expressions equivalent to equation 13.3 do not exist for all coordinates. For example, in the C_2 operation, the x_{H1} coordinate becomes the x_{H2} coordinate in the opposite direction, not a constant times the original x coordinate. Thus, imposing the C_2 operation on H_2O moves the x coordinate of H1 to the x coordinate of H2, implying a 0 in the 9 × 9 matrix in the appropriate diagonal position and a 1 in the 9 × 9 matrix in an off-diagonal position. The behavior of the other coordinates upon operation of C_2, or any other symmetry operation, can be analyzed similarly. Therefore, finding a simpler representation than a 9 × 9 matrix is not as simple as defining an equation like 13.3 for all symmetry operations.

An inspection of the 9 × 9 matrices in equation 13.2 does show a pattern, however. In each 9 × 9 matrix is a repeating 3 × 3 "submatrix" that has a certain set of diagonal elements. In the cases of E and $\sigma(yz)$, these 3 × 3 "submatrices" lie on the main diagonal of the original matrix. In the cases of C_2 and $\sigma(xz)$, some of these 3 × 3 matrices do not lie along the main diagonal of the original matrix. But at least we have identified some characteristic of each 9 × 9 matrix. Recognizing this pattern gives us a way to simplify the matrix representation of the symmetry operation.

To simplify the representation, one needs to identify the *smallest square "submatrix" pattern* that occurs in the same place for *all* matrix representations of the symmetry operations. The numbers will be on the main diagonal of these smaller submatrices. The blocks may have nonzero off-diagonal elements or sometimes zeros for diagonal elements; that doesn't matter. In the example above, a 3 × 3 section in the middle of each matrix, in the same position in each matrix, will serve. In the case of E, the block is outlined as follows:

$$\begin{bmatrix} \begin{matrix}1&0&0\\0&1&0\\0&0&1\end{matrix} & \begin{matrix}0&0&0\\0&0&0\\0&0&0\end{matrix} & \begin{matrix}0&0&0\\0&0&0\\0&0&0\end{matrix}\\ \begin{matrix}0&0&0\\0&0&0\\0&0&0\end{matrix} & \left\{\begin{matrix}1&0&0\\0&1&0\\0&0&1\end{matrix}\right\} & \begin{matrix}0&0&0\\0&0&0\\0&0&0\end{matrix}\\ \begin{matrix}0&0&0\\0&0&0\\0&0&0\end{matrix} & \begin{matrix}0&0&0\\0&0&0\\0&0&0\end{matrix} & \begin{matrix}1&0&0\\0&1&0\\0&0&1\end{matrix} \end{bmatrix} \tag{13.4}$$

The corresponding sections of all 9 × 9 representations above contain the characteristic 3 × 3 submatrix for each particular symmetry operation.

Consider the set of numbers along the main diagonal for one coordinate for all the symmetry operations. (For example, consider the set of numbers corresponding to the behavior of the x coordinate for each of the four symmetry operations.) What we find is that only a certain number of possible sets of numbers for any system has this point group symmetry. Consider the symmetry operations for C_{2v} $[E, C_2, \sigma_v(xz), \sigma_v(yz)]$ from the representations above. We find the following possible sets of numbers: $(1, -1, 1, -1)$, $(1, -1, -1, 1)$, and $(1, 1, 1, 1)$ for any coordinate. These are the only sets of numbers represented in the 9 × 9 matrix representation for the symmetry operations of H_2O. The C_{2v} point group has one more possible set of numbers, which

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*It might help to think of equation 13.3 as an eigenvalue equation, with 1 being the eigenvalue of the operator E. Although this is a good analogy, it applies strictly only for groups in which the "eigenvalue" for E is 1.

would be found if a larger C_{2v} molecule were used as an example. That set would be (1, 1, − 1, −1). Together, these four sets of numbers represent the simplest way of defining the symmetry properties of any object that has C_{2v} symmetry. They are the *irreducible representations* of the C_{2v} point group. The numbers themselves are called *characters.* These characters are not always 1 or −1. They can be zero, a larger integer (2 and 3 are common for higher-symmetry point groups), fractions, or exponential functions. Every point group has a limited number of irreducible representations, each of which is given some label that refers to that irreducible representation. These representations are tabulated in *character tables.* Appendix 3 contains character tables that list not only the symmetry operations of the point groups, but the characters that represent the simplest representation of the effects of those symmetry operations.

Each irreducible representation is labeled with a letter (such as *A*, *B*, *E*, *T*, depending on the character of the identity operation), which sometimes has a subscript, superscript, or primes (′ or ″) with it. All of the irreducible representations within a point group have different labels. Each label represents the set of characters in that row of the table. Sometimes irreducible representations from different point groups have the same label, but it is important to understand that a certain label represents a specific set of characters for a particular point group. Hence, the A_2 irreducible representation in C_{2v} is a different set of characters from the A_2 irreducible representation in D_{4d}. It is necessary that you be aware of what point group you are working in when you use the labels of the irreducible representations.

In many point groups, some of the symmetry operations have the same characters for all of the irreducible representations. They are grouped together into the same *class.* For example, in C_{3v} (the point group that describes the symmetry of NH_3), the two C_3 symmetry operations are grouped as a class, and the three σ_v's are also grouped in a class. *A point group has only as many irreducible representations as it has classes.* Therefore, C_{2v} has four and only four irreducible representations. C_{3v} has only three. Understand that there are a total of six symmetry operations in C_{3v}, so one *can* write a 3 × 6 C_{3v} character table. (It won't be 6 × 6 because C_{3v} only has three irreducible representations.) However, many of the columns will be duplicates, so it is easier to list symmetry operations by class.

Example 13.6

Write the 3 × 6 character table for C_{3v}.

Solution

Using the 3 × 3 character table from Appendix 3 and separating the operations of each class:

	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
A_1	1	1	1	1	1	1
A_2	1	1	1	−1	−1	−1
E	2	−1	−1	0	0	0

As you can see, it is simply more efficient to group the classes together in the character table.

Characters of the irreducible representations of a particular point group can be multiplied by each other. The reason for doing this will be obvious shortly. However, only characters of the *same symmetry operations* are multiplied together. For example, within a certain point group, we will multiply the character of, say, C_3 of the A_2 representation by the character of C_3 of the E_1 representation, but we won't multiply the character of C_3 with the character for, say, σ_h. By performing these multiplications for all classes, it is easy to show that the irreducible representations themselves constitute a mathematical group. For example, the closure requirement is easy to illustrate. Further, if the products of all the symmetry operations of two different irreducible representations were summed up, this sum would be exactly zero. (When doing this, one must include the number of symmetry operations in each class. Otherwise, the form of the character table in Example 13.6 can be used.) A way of stating this is that the irreducible representations of a point group are orthogonal to each other. This is a very useful property of the irreducible representations. The product of the characters of any irreducible representation *with itself* equals h, the order of the point group, which equals the number of symmetry operations in the group. By using the order of the group as a "normalization constant," we can also say that each irreducible representation is *normalized.* Mathematically, using the symbol Γ_a to represent any irreducible representation and the symbol χ_i to represent the individual characters of Γ_a:

$$\frac{1}{h} \cdot \sum_{\substack{\text{all classes} \\ \text{of } \Gamma_a}} N \cdot \chi_i \cdot \chi_j = \begin{cases} 1 \text{ if } i = j \text{ for all } i, j \\ 0 \text{ if } i \neq j \text{ for all } i, j \end{cases} \tag{13.5}$$

where h is the order of the point group and N is the number of symmetry operators in each class. This "orthonormality condition" can be applied to more than two irreducible representations multiplying each other, which we will shortly add as a powerful tool to apply to wavefunctions. Although symmetry operations can be represented by operators, characters are numbers (eigenvalues, actually), and so their multiplication is commutative.

Example 13.7

a. Show that the individual characters for any two different irreducible representations for C_{3v} satisfy the closure property of groups.

b. Show that the sums of the products of the irreducible representations for C_{3v} are orthonormal.

Solution

(a) For the individual characters of E, $2C_3$, and $3\sigma_v$, respectively:

$$A_1 \times A_2 = 1 \times 1 \quad 1 \times 1 \quad 1 \times -1 = 1 \quad 1 \quad -1$$
$$= \text{the } A_2 \text{ irreducible representation}$$

$$A_1 \times E = 1 \times 2 \quad 1 \times -1 \quad 1 \times 0 = 2 \quad -1 \quad 0$$
$$= \text{the } E \text{ irreducible representation}$$

$$A_2 \times E = 1 \times 2 \quad 1 \times -1 \quad -1 \times 0 = 2 \quad -1 \quad 0$$
$$= \text{the } E \text{ irreducible representation}$$

These are the only three combinations, since multiplication of characters is commutative. (A more complete test should include products of the irreducible representations with themselves. Although it is easy to see that $A_1 \times A_1 = A_1$ and $A_2 \times A_2 = A_1$, the product $E \times E$ is not as easy to see. We will have to wait until section 13.7 to show that $E \times E$ does satisfy the closure requirement.)

b. For sums of the products of characters:

$$\frac{1}{h}\cdot\sum_{\text{all classes}} N\cdot\chi_{A_1}\cdot\chi_{A_1} = \frac{1}{6}(1\cdot 1\cdot 1 + 2\cdot 1\cdot 1 + 3\cdot 1\cdot -1)$$

$$= \frac{1}{6}(1 + 2 - 3) = 0$$

$$\frac{1}{h}\cdot\sum_{\text{all classes}} N\cdot\chi_{A_1}\cdot\chi_{E} = \frac{1}{6}(1\cdot 1\cdot 2 + 2\cdot 1\cdot -1 + 3\cdot 1\cdot 0)$$

$$= \frac{1}{6}(2 - 2 + 0) = 0$$

$$\frac{1}{h}\cdot\sum_{\text{all classes}} N\cdot\chi_{A_2}\cdot\chi_{E} = \frac{1}{6}(1\cdot 1\cdot 2 + 2\cdot 1\cdot -1 + 3\cdot -1\cdot 0)$$

$$= \frac{1}{6}(2 - 2 + 0) = 0$$

This shows that the irreducible representations are orthogonal. In addition:

$$\frac{1}{h}\cdot\sum_{\text{all classes}} N\cdot\chi_{A_1}\cdot\chi_{A_1} = \frac{1}{6}(1\cdot 1\cdot 1 + 2\cdot 1\cdot 1 + 3\cdot 1\cdot 1)$$

$$= \frac{1}{6}(1 + 2 + 3) = 1$$

$$\frac{1}{h}\cdot\sum_{\text{all classes}} N\cdot\chi_{A_2}\cdot\chi_{A_2} = \frac{1}{6}(1\cdot 1\cdot 1 + 2\cdot 1\cdot 1 + 3\cdot -1\cdot -1)$$

$$= \frac{1}{6}(1 + 2 + 3) = 1$$

$$\frac{1}{h}\cdot\sum_{\text{all classes}} N\cdot\chi_{\mathrm{E}}\cdot\chi_{\mathrm{E}} = \frac{1}{6}(1\cdot 2\cdot 2 + 2\cdot -1\cdot -1 + 3\cdot 0\cdot 0)$$

$$= \frac{1}{6}(4 + 2 + 0) = 1$$

This shows that the irreducible representations are normalized. Irreducible representations therefore have some of the same properties as wavefunctions.

All point groups have one irreducible representation that has all 1's for characters. This representation is called the *totally symmetric irreducible representation* and is very important in spectroscopy. By convention, it is the first irreducible representation listed in all character tables. Some irreducible representations have 2 or 3 for the character of the E element. (This can be related to degeneracies, in some cases.) Irreducible representations are labeled after a system devised by Robert S. Mulliken. Irreducible representations that have a character for E, χ_E, of 1 are given A or B labels; those that have χ_E equal to 2 are labeled E (not to be confused with the symmetry operation E), and those having χ_E of 3 are labeled T. Subscripts and superscripts are also used to indicate the character with respect to other symmetry operation. The character tables in Appendix 3 use the Mulliken system. Another system, using arbitrarily numbered Greek capital letters gamma, Γ_n, is an older system that is occasionally still seen in the literature.

13.6 Wavefunctions and Symmetry

How does symmetry apply to wavefunctions? First of all, consider the molecule itself. A molecule has a shape that can be described by one of a limited number of groups of symmetry operations. Such groups contain anywhere from one symmetry operation (C_1, which has E) to many (O_h, which has 48) to infinite ($C_{\infty h}$ and $D_{\infty v}$, for example, have an infinite number of σ_v planes of symmetry).

Wavefunctions of molecules span the entire molecule. This is true even though we tend to picture localized electrons in molecules, as in a covalent bond between two atoms. However, strictly speaking, wavefunctions cover—and so the electron exists over—the entire molecule. (In approximations, many molecular orbitals may have a very large, almost-unity value for a single atomic orbital in a linear combination of atomic orbitals, but the basic truth is that all orbitals are molecular orbitals.) If molecules have a shape, then the molecular orbitals must have the same shape. This demands that the molecular *wavefunctions must have the same symmetry properties as the molecule.* We have noted that there are a limited number of combinations of characters for the symmetry operations within a point group. Wavefunctions of a molecule must also have some behavior with respect to the symmetry operations of the point group. The symmetry behavior of a wavefunction must correspond to one of the irreducible representations of the point group. It is typical to label a wavefunction with the symbol for that irreducible representation, just as it is to label the wavefunction with its quantum numbers. Further, the character of the E symmetry operation for a wavefunction is the same as the degeneracy of the wavefunction. A review of the character tables in Appendix 3 shows that a molecule must have at least a C_3 axis in order to have doubly degenerate wavefunctions, and more than one highest-order axis in order to have triply degenerate wavefunctions (although this condition does not guarantee a T irreducible representation).

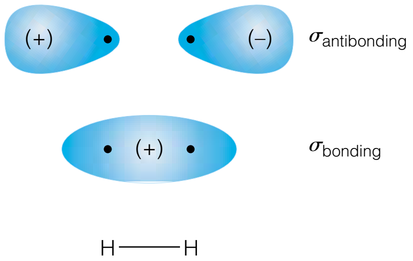

Figure 13.19 A nonrigorous but illustrative representation of the bonding and antibonding σ orbitals of H_2^+. See Example 13.8.

Example 13.8

Figure 13.19 shows a diagram of the σ_{bonding} and $\sigma_{\text{antibonding}}$ orbitals of H_2^+. Assuming that the χ_E is 1 for both, determine the irreducible representations for each molecular orbital. Assume the highest-order axis is the z-axis.

Solution

The symmetry of H_2^+ is $D_{\infty h}$. Upon operation of the diagram of the bonding orbital with all symmetry operations, one finds that the character for each operator is 1 (that is, the same orientation of the orbital is reproduced). This means that the characters for all operations are 1 and so the wavefunction's label is A_{1g} (or Σ_g^+). For the antibonding orbital, inversion through the center yields a wavefunction that has the negative value of the original Ψ. A sign change also occurs upon operation of the C_2 and S_ϕ operations. (You should satisfy yourself that this is the case, using Figure 13.19.) Therefore, the antibonding wavefunction can be labeled with the A_{1u} (or Σ_u^+) irreducible representation.

Wavefunctions can be labeled with appropriate irreducible representation labels. Therefore, the wavefunction of the bonding molecular orbital for H_2^+ would be labeled A_{1g} (that is, $\Psi_{A_{1g}}$). Another phrase that means "irreducible representations" is *symmetry species.* We say that the symmetry species of this wavefunction is A_{1g}.

As we saw briefly in the previous chapter, perhaps the simplest way to represent a molecular orbital is to base it on the atomic orbitals of the atoms involved in the bonding, generally as a linear combination of atomic orbitals (LCAO-MO). Because a wavefunction has symmetry restraints imposed on it, the thought of taking a linear combination of atomic orbitals to represent a molecular orbital becomes a little more tricky, now that linear combination must have the correct symmetry. Such a requirement suggests that we should not use just any linear combination of atomic orbitals, although we can. It would be better to use some *symmetry-adapted linear combinations* (SALCs) of atomic orbitals, in order to take advantage of group theory and symmetry considerations. Before we construct SALCs, we must introduce one powerful tool of group theory.

13.7 The Great Orthogonality Theorem

We showed above that individual symmetry species are orthogonal to each other. This is a consequence of a more general statement of group theory called the *great orthogonality theorem* (GOT, sometimes called the grand orthogonality theorem). The GOT is a general relationship between *all* of the matrix elements of a representation of a symmetry operation (like the matrices in equation 13.2). Here, we will focus on the application of the GOT to the *characters* of the irreducible representations, which will be much simpler than considering all of the matrix elements.

Since wavefunctions are being combined in linear combinations, one can also take linear combinations of the irreducible representations and their characters. However, it is more common to be able to determine the set of characters that represents the entire linear combination, instead of its constituent parts. This set of characters is almost always a reducible representation. The question is, what is the linear combination in terms of the irreducible representations? How many A_1's in the combination, how many B_1's, how many E's? We can apply the great orthogonality theorem to determine the specific content (that is, the number of each irreducible representation) of a set of characters that represent a linear combination. We will use the capital Greek letter gamma, Γ, to represent any one of the irreducible representations of a point group. The number of contributions any particular Γ has to a reducible representation is given by the following formula:

$$a_\Gamma = \frac{1}{h} \sum_{\substack{\text{all classes} \\ \text{of } \Gamma\text{a}}} N \cdot \chi_\Gamma \cdot \chi_{\text{linear combo}} \tag{13.6}$$

where a_Γ is the number of times the irreducible representation Γ appears in the linear combination, h is the order of the group, N is the number of operations in each class, χ_Γ is the character of the class of that irreducible representation (from the character table), and $\chi_{\text{linear combo}}$ is the character of the class for the linear combination. Note that this is similar to the expression in equation 13.5. Example 13.9 shows how to apply this equation.

Example 13.9

The following set of characters is for a linear combination of irreducible representations for a system having $C_{3\text{v}}$ symmetry (say, ammonia):

	E	$2C_3$	$3\sigma_\text{v}$
Γ_combo	7	1	1

Use equation 13.6 to determine what linear combination of A_1, A_2, and E symmetry species is being represented.

Solution

We need the characters for A_1, A_2, and E from the character table of the $C_{3\text{v}}$ point group. For the number of times A_1 appears in the linear combination,

$$a_{A_1} = \frac{1}{6} \sum_{\text{all classes}} N \cdot \chi_{A_1} \cdot \chi_{\text{linear combo}}$$

where the summation has three terms. Solving:

$$a_{A_1} = \frac{1}{6}\left\{ \underbrace{\underbrace{1}_{N} \cdot \overbrace{1}^{\substack{\chi_{A_1}\text{, from} \\ \text{character table}}} \cdot \underbrace{7}_{\chi_{\text{linear combo}}}}_{\text{term for } E} + \underbrace{2 \cdot 1 \cdot 1}_{C_3} + \underbrace{3 \cdot 1 \cdot 1}_{\sigma_\text{v}} \right\}$$

$$a_{A_1} = \frac{1}{6}(7 + 2 + 3) = \frac{1}{6}(12) = 2$$

so that the A_1 symmetry species appears twice in the linear combination. Similarly, for A_2 and E:

$$a_{A_2} = \tfrac{1}{6}[(1 \cdot 1 \cdot 7) + (2 \cdot 1 \cdot 1) + (3 \cdot -1 \cdot 1)] = \tfrac{1}{6}(6) = 1$$

$$a_E = \tfrac{1}{6}[(1 \cdot 2 \cdot 7) + (2 \cdot -1 \cdot 1) + (3 \cdot 0 \cdot 1)] = \tfrac{1}{6}(12) = 2$$

Therefore, this Γ_combo is a sum of two A_1, one A_2, and two E symmetry species. This is how the great orthogonality theorem is applied to reduce character sets into their unique set of irreducible representations.

The mathematical way of illustrating the above combination of symmetry species is to use the $\oplus$ sign instead of a $+$ sign (which is how linear combinations are usually expressed). One can therefore write Γ_combo from above as

$$\Gamma_\text{combo} = 2A_1 \oplus 1A_2 \oplus 2E$$

The great orthogonality theorem is useful because it allows us to break down any reducible representation into its irreducible representations. Once any scheme for determining a representation for a wavefunction is applied, the GOT can be used to reduce the representation into its irreducible components. For example, in the case of the $R_\text{h}(3)$ spherical point group, the characters are given as expressions in terms of the angle ϕ of the particular rotation. The characters for any one representation are transferable to the symmetry operations of any other point group, which ultimately represent a *reducible* representation in the new point group. Using the GOT, one determines the symmetry labels of the representation in the new point group. An example is electron subshells. The quantum number ℓ defines which irreducible representation a set of wavefunctions belongs to in the $R_h(3)$ point group, the ℓth representation. One must also determine whether the wavefunction is positive or negative with respect to inversion, which determines whether the label "g" or "u" is applicable to the irreducible representation. One then determines the characters in $R_h(3)$, transfers those characters to the symmetry operations of a new point group, and using the GOT determines the symmetry labels of the $2\ell + 1$ orbitals of that subshell. The following example illustrates how this might be done.

Example 13.10

Determine the symmetry labels of the hydrogen-like *p* orbitals in T_d symmetry.

Solution

For *p* orbitals, $\ell = 1$, and the sign on the *p* orbitals changes upon inversion, so the character for inversion should be negative. In $R_h(3)$, the irreducible representation for *p* orbitals is therefore $D_u^{(1)}$. Using the formulas for the characters for the symmetry operations, we can calculate what the characters are for T_d [see the character table for $R_h(3)$]:

$$\chi_E = 3$$

$$\chi_{C_3} = 1 + 2\cos\theta = 1 + 2\cos(120°) = 0$$

$$\chi_{C_2} = 1 + 2\cos\theta = 1 + 2\cos(180°) = -1$$

$$\chi_{S_4} = 1 - 2\cos\theta = 1 - 2\cos(90°) = 1$$

$$\chi_{\sigma_d} = -1$$

Since T_d does not have a center of inversion, the formula for *i* is not needed. The characters for the *p* orbitals are thus

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ	3	0	-1	1	-1

Using the great orthogonality theorem, we can determine what linear combination of irreducible representations of the T_d point group this is. One finds:

$$a_{A_1} = \tfrac{1}{24}[(1\cdot1\cdot3) + (8\cdot1\cdot0) + (3\cdot1\cdot-1) + (6\cdot1\cdot1) + (6\cdot1\cdot-1)]$$
$$= \tfrac{1}{24}(0) = 0$$

$$a_{A_2} = \tfrac{1}{24}[(1\cdot1\cdot3) + (8\cdot1\cdot0) + (3\cdot1\cdot-1) + (6\cdot-1\cdot1) + (6\cdot-1\cdot-1)]$$
$$= \tfrac{1}{24}(0) = 0$$

$$a_E = \tfrac{1}{24}[(1\cdot2\cdot3) + (8\cdot-1\cdot0) + (3\cdot2\cdot-1) + (6\cdot0\cdot1) + (6\cdot0\cdot-1)]$$
$$= \tfrac{1}{24}(0) = 0$$

$$a_{T_1} = \tfrac{1}{24}[(1\cdot3\cdot3) + (8\cdot0\cdot0) + (3\cdot-1\cdot-1) + (6\cdot1\cdot1) + (6\cdot-1\cdot-1)]$$
$$= \tfrac{1}{24}(24) = 1$$

$$a_{T_2} = \tfrac{1}{24}[(1\cdot3\cdot3) + (8\cdot0\cdot0) + (3\cdot-1\cdot-1) + (6\cdot-1\cdot1) + (6\cdot1\cdot-1)]$$
$$= \tfrac{1}{24}(0) = 0$$

The three p orbitals collectively are assigned to a T_1 symmetry species. (This conclusion could have been reached by comparison of Γ to the irreducible representations.) Since the character of the T_1 symmetry species is 3, this indicates that the (hydrogen-like) p orbitals are triply degenerate when a T_d symmetry is imposed on them.

13.8 Using Symmetry in Integrals

The assignment of symmetry species to wavefunctions has some useful consequences for evaluating integrals involving wavefunctions. Consider the integral having the form

$$\int \Psi_{\Gamma 1}^{*} \Psi_{\Gamma 2}\, d\tau \tag{13.7}$$

where $\Gamma 1$ and $\Gamma 2$ represent the symmetry species of each wavefunction of a system that has a certain symmetry. This integral, if it is nonzero, is simply some numerical value. That value does not change if one operates on it with any symmetry operation, so one can say that the character of the symmetry operation on a number is 1. (Consider that $\sigma_v(3) = 1 \cdot 3 = 3$.) Therefore, all numerical values can be assigned to the totally symmetric irreducible representation of any point group. Consider the opposite argument. If that integral is to have a nonzero numerical value, then the irreducible representation of the combination $\Psi^{*}{}_{\Gamma 1}\Psi_{\Gamma 2}$ has to have totally symmetric symmetry. This implies that

$$(\Gamma 1)^{*} \otimes \Gamma 2 = A_1 \tag{13.8}$$

where A_1 in this point group happens to be the totally symmetric irreducible representation, and the symbol $\otimes$ is used to imply the proper multiplication of appropriate characters of each representation. (The complex conjugate in equation 13.8 is rarely invoked, because most characters are real numbers.) If the product of the two irreducible representations is anything other than A_1 (or whatever the totally symmetric representation is), *then the integral must be exactly zero.* This is a powerful tool to determine whether an integral must be zero. (In fact, most combinations of wavefunctions of arbitrary symmetry species are exactly zero from symmetry considerations. This idea drastically simplifies the mathematical considerations of molecular wavefunctions if the wavefunctions have symmetry elements.)

Although equation 13.8 is somewhat general, it does not cover all cases. For example, in symmetry species that have E or T labels, multiplication of the irreducible representations yields a reducible representation that must be reduced using the great orthogonality theorem. In such cases, the integral is identically zero *unless* the reducible representation can be broken down into irreducible representations, one of which must be A_1 (or whatever the totally symmetric representation is). Such a reducible representation is said to "contain" A_1. Mathematically, this is written as

$$(\Gamma 1)^{*} \otimes \Gamma 2 \subset A_1 \tag{13.9}$$

where the symbol $\subset$ means "contains." This is the most applicable statement of the requirement that an integral as in equation 13.7 might be nonzero. If the product of the two irreducible representations does not contain A_1, then the integral *must be zero.*

Example 13.11

Determine whether the following integrals are exactly zero or might be nonzero strictly from symmetry considerations.

a. $\int \Psi_{A_1}^{*}\Psi_{A_2}\,d\tau$ in a T_d molecule
b. $\int \Psi_{A_2}^{*}\Psi_{E}\,d\tau$ in a C_{3v} molecule
c. $\int \Psi_{E}^{*}\Psi_{E}\,d\tau$ in a D_{2d} molecule

Solution

In each case, the characters of the irreducible representations must be multiplied together and the product evaluated for the presence of the totally symmetric representation of the respective point group.

a. In T_d, $A_1 \otimes A_2 = A_2$, which is not the totally symmetric representation. Therefore the integral must be exactly zero.

b. In C_{3v}, $A_2 \otimes E = E$, which is not the totally symmetric representation. Therefore the integral must be exactly zero.

c. In D_{2d}, $E \otimes E$ yields a set of characters

	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$
$E \otimes E$	4	0	4	0	0

This is not an irreducible representation and so must be broken down using the GOT. One can show by applying equation 13.6 that

$$E \otimes E = A_1 \oplus A_2 \oplus B_1 \oplus B_2$$

which does contain A_1. Therefore this integral may be nonzero. This is not a guarantee that it is nonzero, but there is no symmetry reason requiring that it be exactly zero.

As in the above example, simple symmetry considerations easily show many integrals of wavefunctions to be exactly zero. This idea can be simplified further for some conditions. For the product of only two irreducible representations, *the integral will be exactly zero unless both functions are of the same symmetry species.* In integrals that are combinations of more than two functions (that is, two wavefunctions and an operator), the combination of two must yield a resulting symmetry species that is the same as the third. Otherwise, the integral is exactly zero. In showing this, it does not matter which two symmetry species are combined. Thus, if symmetry considerations are applied first, many integrals can be shown to be identically zero and will not even have to be evaluated.

Example 13.12

For a hydrogen atom whose symmetry is described by the $R_h(3)$ point group, the 1*s* orbital has the irreducible representation label $D_g^{(0)}$. The 2*s* orbital also has the irreducible representation label $D_g^{(0)}$. The electromagnetic (EM) radiation operator that causes an electron to go from the 1*s* state to any other state has the irreducible representation $D_u^{(1)}$. Show that the integral

$$\int \Psi_{1s}^{*} \cdot (\text{EM radiation operator}) \cdot \Psi_{2s} \cdot d\tau$$

is exactly zero, implying that this electronic transition will not occur. You do not need to consider the symmetry properties of the form of $d\tau$. You will have to consult the character table for the $R_h(3)$ point group.

Solution

The following table is taken from the $R_h(3)$ character table:

	E	C_ϕ	i	$S_{-\phi}$	σ
$\chi_{1s} = D_g^{(0)}$	1	1	1	1	1
$\chi_{2s} = D_g^{(0)}$	1	1	1	1	1
$\chi_{\text{EM op}} = D_u^{(1)}$	3	$1 + 2\cos\phi$	-3	$-1 + 2\cos\phi$	1

The product of any two rows must be equal to or contain the third, else the integral must be exactly zero by symmetry arguments. It is easiest to determine the product $\chi_{1s} \times \chi_{2s}$, which are all simply 1×1 for each symmetry operation. Therefore, we are comparing the two sets of characters:

	E	C_ϕ	i	$S_{-\phi}$	σ
$\chi_{1s} \times \chi_{2s}$	1	1	1	1	1
$\chi_{\text{EM op}}$	3	$1 + 2\cos\phi$	-3	$-1 + 2\cos\phi$	1

Clearly, 1 does not equal 3 (for the character of E). Clearly, 1 does not equal $1 + 2\cos\phi$ for all values of ϕ (which would be required); and so forth. Therefore, by showing that $\chi_{1s} \times \chi_{2s}$ does not equal $\chi_{\text{EM op}}$, we can say that the integral

$$\int \Psi_{1s}^* \cdot (\text{EM radiation operator}) \cdot \Psi_{2s} \cdot d\tau$$

is exactly zero. We will find in a later chapter that this is what defines a *forbidden transition.*

Symmetry considerations are especially useful in spectroscopy, where the operator can also be assigned some symmetry species of the point group. Polarized light and magnetic fields can be assigned a symmetry species within the point group of the molecule, and whether or not a spectroscopic transition will occur can be determined by the idea embodied in equation 13.9. This is the symmetry basis for *selection rules.* We will cover such topics in the next few chapters.

For linear combinations of wavefunctions, the symmetry species of the individual wavefunctions is very important. One ramification of symmetry considerations is that wavefunctions of different symmetry species do not *combine* to, say, make bonds. Since we are seeking linear combinations of atomic wavefunctions, this allows us to conclude that the only useful combinations for molecules will be of those atomic wavefunctions that belong to the same symmetry species of the molecule. The construction of symmetry-adapted linear combinations utilizes this simplifying idea.

13.9 Symmetry-Adapted Linear Combinations

By keeping symmetry in mind, it is possible to construct appropriate combinations of atomic orbital wavefunctions to approximate molecular orbital wavefunctions that cover, or *span,* the entire molecule. The use of symmetry is the first real restriction we have placed on linear combinations, but it makes sense. After all, it serves no purpose to use a p_x atomic orbital in a linear combination of a molecular orbital when the chemical bond points in the z direction. *Symmetry-adapted linear combinations* (SALCs) are more intuitively correct approximations than any random combination of atomic orbitals.

Character tables and the GOT are crucial elements in determining a proper SALC of atomic orbitals. The first step is to identify the correct point group of the molecule, because the wavefunction that describes any molecular orbital must also have this symmetry. The second step is to identify all of the atomic orbitals that are being considered for the molecular orbitals. Typically, the necessary atomic orbitals are those that are occupied in the atoms themselves. We must not forget that there exist three independent *p* orbitals, five independent *d* orbitals, and so on, that can contribute to the bonding. All such orbitals must be considered. For example, in considering the atomic orbitals that make up the molecular orbitals of H_2O, we include the 1*s* atomic orbital of hydrogen 1, the 1*s* orbital of hydrogen 2, the 1*s* orbital of O, the 2*s* orbital of O, and the $2p_x$, $2p_y$, and $2p_z$ orbitals of the O atom. A total of *seven* individual atomic orbitals are used.

It should be understood that only atomic orbitals that belong to the same symmetry species will combine. At first glance, it can be challenging to determine which atomic orbitals belong to the same symmetry species, and it may also be challenging to identify all of the atomic orbitals of any one irreducible representation. It is sometimes easier to include all atomic orbitals in an initial treatment. They will separate themselves into the proper groupings when the symmetry requirements are imposed. Therefore, in the following examples all of the atomic orbitals will be considered. In the end, we will see how the atomic orbitals are separated by their symmetry species. (With practice, separation of atomic orbitals by symmetry species becomes obvious; however, in the beginning, it may seem nonsensical. This is why the more complete treatment is introduced here.) Determination of SALCs follows a sort of recipe. We will not go into the specific group theory derivation of the procedure, but there is mathematical justification for the following steps.

1. Determine which atomic orbitals will be used.
2. Make a table that has each individual atomic orbital listed on one side (say, the left) and the symmetry operations listed on a perpendicular side. List the symmetry operations *individually,* not by class. There are *h* symmetry operations in the point group, where *h* is the order of the group. There should therefore be *h* entries for the symmetry operations.
3. Operate on each individual atomic orbital with each symmetry operation and write the result in the table. The result will be either (1) the orbital itself or the negative of the orbital itself or, rarely, some fraction of itself, or (2) some other orbital or the negative of some other orbital or, rarely, some fraction of another orbital, or (3) not correspond to the position of any other orbital in the molecule, in which case the result is zero. The table should be completely filled when finished.
4. Consult the character table of the point group of the molecule. (Note that in step 2 we have constructed our own table to mimic the structure of the character table.) Consider each irreducible representation in the character table. For each individual symmetry operation (you may have to separate classes of symmetry operations), multiply the character by the result of the corresponding symmetry operation in each row of your table.
5. Add all of these products in each *column,* giving you *h* sums. Multiply each sum by a normalization factor of $1/h$ (h = order of group). The resulting expressions are the SALCs, which will have the symmetry properties of that irreducible representation.

6. Do this for all irreducible representations of the point group. This will yield a large number of linear combinations. Inspect them, for some of them may be equivalent and so all but one of them can be ignored. Others may be linear combinations of two (or more) SALCs, and so are not mathematically independent. Only the unique combinations should be considered further. (The choice of which are the unique combinations is often a matter of preference and not an absolute.)

The following example is based on the six preceding steps.

Example 13.13

Determine the symmetry-adapted linear combinations for the molecular orbitals of H_2O using the atomic orbitals of H1, H2, and O. (The numbers on the H's are labels for identification purposes only.)

Solution

H_2O has C_{2v} symmetry. Each step from the list above is labeled.

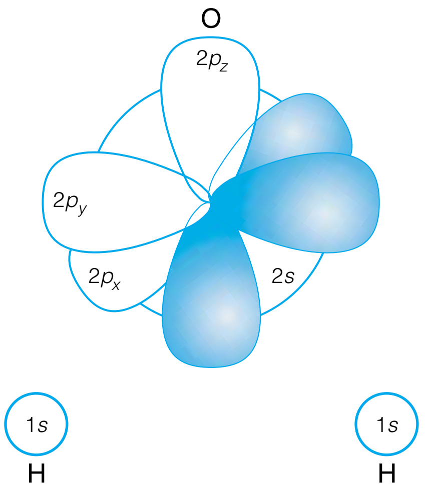

Figure 13.20 The valence atomic orbitals used to construct symmetry-adapted linear combination molecular orbitals of H_2O. Although the atomic orbitals do not have C_{2v} symmetry, the proper combinations of atomic orbitals will. See Example 13.13.

1. The atomic orbitals used to make the SALCs were identified above and will be labeled $1s_{\mathrm{H1}}$, $1s_{\mathrm{H2}}$, $1s_{\mathrm{O}}$, $2s_{\mathrm{O}}$, $2p_{x,\mathrm{O}}$, $2p_{y,\mathrm{O}}$, and $2p_{z,\mathrm{O}}$. These orbitals are illustrated in Figure 13.20.
2. The following table can be set up:

	$1s_{\mathrm{H1}}$	$1s_{\mathrm{H2}}$	$1s_{\mathrm{O}}$	$2s_{\mathrm{O}}$	$2\,p_{x,\mathrm{O}}$	$2p_{y,\mathrm{O}}$	$2p_{z,\mathrm{O}}$
E							
C_2							
σ_v							
σ'_v							

3, 4. The E symmetry operation does not change the orbitals. The C_2 and σ'_v operations switch the hydrogen $1s$ orbitals and have varying effects on the oxygen's orbitals. The σ_v does not affect the hydrogen orbitals but does have the effect of reversing the $2p_{y,\mathrm{O}}$ orbital. Each symmetry result is multiplied by the character for the symmetry operation of that irreducible representation. For the A_1 symmetry species, we get the following:

	$1s_{\mathrm{H1}}$	$1s_{\mathrm{H2}}$	$1s_{\mathrm{O}}$	$2s_{\mathrm{O}}$	$2p_{x,\mathrm{O}}$	$2p_{y,\mathrm{O}}$	$2p_{z,\mathrm{O}}$
E	$1 \cdot 1s_{\mathrm{H1}}$	$1 \cdot 1s_{\mathrm{H2}}$	$1 \cdot 1s_{\mathrm{O}}$	$1 \cdot 2s_{\mathrm{O}}$	$1 \cdot 2p_{x,\mathrm{O}}$	$1 \cdot 2p_{y,\mathrm{O}}$	$1 \cdot 2p_{z,\mathrm{O}}$
C_2	$1 \cdot 1s_{\mathrm{H2}}$	$1 \cdot 1s_{\mathrm{H1}}$	$1 \cdot 1s_{\mathrm{O}}$	$1 \cdot 2s_{\mathrm{O}}$	$1 \cdot -2p_{x,\mathrm{O}}$	$1 \cdot -2p_{y,\mathrm{O}}$	$1 \cdot 2p_{z,\mathrm{O}}$
σ_v	$1 \cdot 1s_{\mathrm{H1}}$	$1 \cdot 1s_{\mathrm{H2}}$	$1 \cdot 1s_{\mathrm{O}}$	$1 \cdot 2s_{\mathrm{O}}$	$1 \cdot 2p_{x,\mathrm{O}}$	$1 \cdot -2p_{y,\mathrm{O}}$	$1 \cdot 2p_{z,\mathrm{O}}$
σ'_v	$1 \cdot 1s_{\mathrm{H2}}$	$1 \cdot 1s_{\mathrm{H1}}$	$1 \cdot 1s_{\mathrm{O}}$	$1 \cdot 2s_{\mathrm{O}}$	$1 \cdot -2p_{x,\mathrm{O}}$	$1 \cdot 2p_{y,O}$	$1 \cdot 2p_{z,\mathrm{O}}$

Since the A_1 irreducible representation has all 1's for characters, the results of the symmetry operations on the atomic orbitals are all being multiplied by 1.

5. Summing the terms in each column, we get seven linear combinations, which are in order:

$$\Psi_{A_1} = \tfrac{1}{4}(1s_{\mathrm{H1}} + 1s_{\mathrm{H2}} + 1s_{\mathrm{H1}} + 1s_{\mathrm{H2}})$$

$$\Psi_{A_1} = \tfrac{1}{4}(1s_{\mathrm{H2}} + 1s_{\mathrm{H1}} + 1s_{\mathrm{H2}} + 1s_{\mathrm{H1}})$$

$$\Psi_{A_1} = \tfrac{1}{4}(1s_{\mathrm{O}} + 1s_{\mathrm{O}} + 1s_{\mathrm{O}} + 1s_{\mathrm{O}})$$

$$\Psi_{A_1} = \tfrac{1}{4}(2s_\mathrm{O} + 2s_\mathrm{O} + 2s_\mathrm{O} + 2s_\mathrm{O})$$

$$\Psi_{A_1} = \tfrac{1}{4}(2p_{x,\mathrm{O}} - 2p_{x,\mathrm{O}} + 2p_{x,\mathrm{O}} - 2p_{x,\mathrm{O}})$$

$$\Psi_{A_1} = \tfrac{1}{4}(2p_{y,\mathrm{O}} - 2p_{y,\mathrm{O}} - 2p_{y,\mathrm{O}} + 2p_{y,\mathrm{O}})$$

$$\Psi_{A_1} = \tfrac{1}{4}(2p_{z,\mathrm{O}} + 2p_{z,\mathrm{O}} + 2p_{z,\mathrm{O}} + 2p_{z,\mathrm{O}})$$

The first and second combinations are the same (the terms are simply listed in different order), and the fifth and sixth combinations are exactly zero. The unique wavefunctions are, after some algebraic simplification:

$$\Psi_{A_1} = \tfrac{1}{2}(1s_\mathrm{H1} + 1s_\mathrm{H2})$$

$$\Psi_{A_1} = 1s_\mathrm{O}$$

$$\Psi_{A_1} = 2s_\mathrm{O}$$

$$\Psi_{A_1} = 2p_{z,\mathrm{O}}$$

6. Analogous steps will yield proper wavefunctions with A_2, B_1, and B_2 symmetries. They ultimately yield, for the unique combinations,

$$\Psi_{B_1} = \tfrac{1}{2}(1s_\mathrm{H1} - 1s_\mathrm{H2})$$

$$\Psi_{B_1} = 2p_{x,\mathrm{O}}$$

$$\Psi_{B_2} = 2p_{y,\mathrm{O}}$$

There are no nonzero linear combinations that can be labeled with the A_2 symmetry species. Although most of the molecular wavefunctions are represented by a single atomic wavefunction in this case, this will not always be so. We get seven unique molecular orbitals from the seven atomic orbitals.

Electron spins are not addressed explicitly by MO theory, but they are treated with respect to the Pauli principle just as atomic orbitals are: only two electrons can occupy any one orbital, and their spins must be opposite. Just as in atoms, electrons in molecules fill MOs starting with the lowest-energy MO, and in order of increasing energy. If two or more MOs are degenerate, one electron fills each MO before pairing of electrons in orbitals (Hund's rule).

13.10 Valence Bond Theory

Previously, we have treated orbitals as covering the molecule as a whole, and have not from the start restricted the orbitals to any one atom. Many molecular orbitals can be approximated as linear combinations of atomic orbitals. Another way to consider molecular wavefunctions is in terms of *products* of atomic orbitals. This is *valence bond theory,* and ultimately it is very useful for describing the structures of molecules. Valence bond (or VB) theory dates from 1927, when W. Heitler and F. W. London constructed the first successful quantum-mechanical approximation of the hydrogen molecule, H_2. It was developed further by J. C. Slater (of Slater determinant fame) and Linus Pauling.

We will use the hydrogen molecule as an example. At infinite interatomic separation, each hydrogen atom has its own independent wavefunction:

$$\Psi_\mathrm{H1} \equiv 1s_\mathrm{H1}(1)$$

$$\Psi_\mathrm{H2} \equiv 1s_\mathrm{H2}(2)$$

where the individual hydrogens *and* their electrons are labeled as either 1 or 2. (It is important to keep track of the labels 1 and 2. They will independently refer to the atom and the electron.) The wavefunction of the complete system (that is, the two individual hydrogen atoms) is the product of the two individual wavefunctions:

$$\Psi_{\text{system}} = \Psi_{\text{H1}} \cdot \Psi_{\text{H2}} = 1s_{\text{H1}}(1) \cdot 1s_{\text{H2}}(2) \qquad \textbf{(13.10)}$$

where we are assuming that each hydrogen atom has its electron in the $1s$ atomic orbital. When the two atoms come together to make a hydrogen molecule, it is assumed that the wavefunction of the molecule also has this sort of wavefunction. But in the molecule, the individual electrons aren't tied down to one particular nucleus. Another possible product of wavefunctions might be $1s_{\text{H1}}(2) \cdot 1s_{\text{H2}}(1)$, where each electron is now associated with the other hydrogen atom. As done previously with multiple possible wavefunctions, we consider that the best wavefunction is a linear combination of the individual wavefunctions:

$$\Psi_{\text{system}} = \frac{1}{\sqrt{2}}[1s_{\text{H1}}(1) \cdot 1s_{\text{H2}}(2) \pm 1s_{\text{H1}}(2) \cdot 1s_{\text{H2}}(1)] \qquad \textbf{(13.11)}$$

where $1/\sqrt{2}$ is a normalization factor for the linear combination. Equation 13.11 actually represents two possible wavefunctions, one being the sum and the other the difference of the two product wavefunctions. There are two additional concerns, however: spin and the Pauli principle. Spin functions must be included with spatial functions for a complete wavefunction. The Pauli principle also requires that the complete wavefunction be antisymmetric upon the exchange of the two electrons [that is, $\Psi(1, 2) = -\Psi(2, 1)$]. So in each of the wavefunctions in equation 13.11, a spin function must be included *and* the spin function must be of the proper form so that the complete wavefunction is antisymmetric with respect to exchange of the two electrons.

There are several possible forms for the spin function of the molecule. Because there are two electrons, we are going to have to number the spin functions with the electron number to keep track of which electron has what spin function. One possible molecular spin function is for both electrons to have the α spin function. The molecular spin function is thus $\alpha(1)\alpha(2)$. Or, they could both have β spin functions: the molecular spin function is then $\beta(1)\beta(2)$. Or, one electron can have the α function and the other the β function, but which? Remember that individual electrons are indistinguishable from each other. Just as for the spatial wavefunction in equation 13.11, there are two possible combinations of α and β spin functions, $\alpha(1)\beta(2)$ and $\alpha(2)\beta(1)$. The most appropriate wavefunction is the linear combination of the two: $(1/\sqrt{2})[\alpha(1)\beta(2) \pm \alpha(2)\beta(1)]$. Again, note that the $\pm$ sign means that there are two separate functions here. These are the four possibilities for the spin part of the total wavefunction. These possibilities must be combined with the spatial wavefunctions in equation 13.11 to make antisymmetric wavefunctions for H_2.

Since symmetric and antisymmetric properties follow the same rules of multiplication as odd/even or positive/negative multiplication (that is, sym × sym = sym, sym × antisym = antisym, antisym × antisym = sym), all we need to do is identify the symmetry properties of the spatial and spin wavefunctions and combine antisymmetric parts with symmetric parts to get an overall antisymmetric wavefunction. The following summarizes the properties, which can easily be verified:

$$\Psi_{\text{spatial}} = \frac{1}{\sqrt{2}}[1s_{\text{H1}}(1) \cdot 1s_{\text{H2}}(2) + 1s_{\text{H1}}(2) \cdot 1s_{\text{H2}}(1)] \quad \text{symmetric}$$

$$\Psi_{\text{spatial}} = \frac{1}{\sqrt{2}}[1s_{\text{H1}}(1) \cdot 1s_{\text{H2}}(2) - 1s_{\text{H1}}(2) \cdot 1s_{\text{H2}}(1)] \quad \text{antisymmetric}$$

$$\alpha(1)\alpha(2) \quad \text{symmetric}$$

$$\beta(1)\beta(2) \quad \text{symmetric}$$

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad \text{symmetric}$$

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad \text{antisymmetric}$$

The symmetric spatial function is combined with the antisymmetric spin function to make a single antisymmetric total wavefunction for H_2. Since the energy of the molecule depends on the *spatial* wavefunction, this combination represents a state that has a degeneracy of 1 and so is called a *singlet* state. The antisymmetric spatial function can be combined with three symmetric spin functions to make three additional and individual antisymmetric total wavefunctions for H_2. Again, since the total energy depends almost entirely on the spatial part of the wavefunction, these three different wavefunctions have the same energy, and so these represent an energy level for H_2 that has a degeneracy of 3. It is called a *triplet* state. The complete wavefunctions are

$$^{1}\Psi_{\text{H}_2,\text{valence}} = \frac{1}{\sqrt{2}}[1s_{\text{H1}}(1) \cdot 1s_{\text{H2}}(2) + 1s_{\text{H1}}(2) \cdot 1s_{\text{H2}}(1)] \cdot \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

$$^{3}\Psi_{\text{H}_2,\text{valence}} = \begin{cases} \frac{1}{\sqrt{2}}[1s_{\text{H1}}(1) \cdot 1s_{\text{H2}}(2) - 1s_{\text{H1}}(2) \cdot 1s_{\text{H2}}(1)] \cdot \alpha(1)\alpha(2) \\ \frac{1}{\sqrt{2}}[1s_{\text{H1}}(1) \cdot 1s_{\text{H2}}(2) - 1s_{\text{H1}}(2) \cdot 1s_{\text{H2}}(1)] \cdot \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \\ \frac{1}{\sqrt{2}}[1s_{\text{H1}}(1) \cdot 1s_{\text{H2}}(2) - 1s_{\text{H1}}(2) \cdot 1s_{\text{H2}}(1)] \cdot \beta(1)\beta(2) \end{cases} \quad \textbf{(13.12)}$$

Which state has the lowest energy and represents the ground state? As might be expected, the sum of two negative numbers (recall that the energy of the hydrogen atom itself is negative, due to the attraction of the proton and electron) is lower, or more negative, than the difference of two negative numbers (where the subtraction of a negative yields, ultimately, an addition process). There is also experimental evidence that the lowest-energy state of H_2 is a singlet state. Therefore the singlet wavefunction in equation 13.12 is the approximation of the valence bond theory for the ground state of H_2. The triplet state is, by definition, an excited state.

In evaluating the energy of the wavefunctions in equation 13.12, one can set up a perturbational or variational treatment to come up with some expression for the energy of the molecule. Although we won't do this in its entirety, we will illustrate some parts of it that introduce some unique features of molecular quantum mechanics. Assume that the energy of the ground state is determined solely by the spatial part of the wavefunction. (As mentioned above, this is not a bad approximation.) For the energy of the ground state of H_2, one needs to evaluate

$$\begin{aligned} \mathrm{E}_{\mathrm{H}_2} = \tfrac{1}{2}\int_6 &[1s_{\mathrm{H}1}(1)\cdot 1s_{\mathrm{H}2}(2) + 1s_{\mathrm{H}1}(2)\cdot 1s_{\mathrm{H}2}(1)]^* \\ &\times \hat{H}[1s_{\mathrm{H}1}(1)\cdot 1s_{\mathrm{H}2}(2) + 1s_{\mathrm{H}1}(2)\cdot 1s_{\mathrm{H}2}(1)]\, d\tau_1\, d\tau_2 \end{aligned}$$

where the 6 on the integral sign means that it is a sixfold integration over the three coordinates of electron 1 and the three coordinates of electron 2. This integral can be expanded by multiplying out the terms of the wavefunction. We get four sextuple-integrals

$$\begin{aligned} E_{\mathrm{H}_2} = \tfrac{1}{2}\Bigg[&\int_6 [1s_{\mathrm{H}1}(1)\cdot 1s_{\mathrm{H}2}(2)]^*\hat{H}[1s_{\mathrm{H}1}(1)\cdot 1s_{\mathrm{H}2}(2)\Bigg]\, d\tau_1\, d\tau_2 \\ &+ \int_6 [1s_{\mathrm{H}1}(2)\cdot 1s_{\mathrm{H}2}(1)]^*\hat{H}[1s_{\mathrm{H}1}(1)\cdot 1s_{\mathrm{H}2}(2)]\, d\tau_1\, d\tau_2 \\ &+ \int_6 [1s_{\mathrm{H}1}(1)\cdot 1s_{\mathrm{H}2}(2)]^*\hat{H}[1s_{\mathrm{H}1}(2)\cdot 1s_{\mathrm{H}2}(1)]\, d\tau_1\, d\tau_2 \\ &+ \int_6 [1s_{\mathrm{H}1}(2)\cdot 1s_{\mathrm{H}2}(1)]^*\hat{H}[1s_{\mathrm{H}1}(2)\cdot 1s_{\mathrm{H}2}(1)]\, d\tau_1\, d\tau_2 \end{aligned}$$

As complicated as this looks, each term can be broken down into a number of one-electron parts that can be approximated using the known solution for the hydrogen atom. This is very reminiscent of the earlier treatment of the helium atom. But just as for the helium atom, the terms that involve the repulsion between the two electrons cannot be separated and so cannot be evaluated analytically. Those terms, one from each of the integrals above, have the following forms:

$$\begin{aligned} &\int_6 [1s_{\mathrm{H}1}(1)\cdot 1s_{\mathrm{H}2}(2)]^*\frac{e^2}{4\pi\epsilon_0 r_{12}^2}[1s_{\mathrm{H}1}(1)\cdot 1s_{\mathrm{H}2}(2)]\, d\tau_1\, d\tau \\ &= \int_6 [1s_{\mathrm{H}1}(2)\cdot 1s_{\mathrm{H}2}(1)]^*\frac{e^2}{4\pi\epsilon_0 r_{12}^2}[1s_{\mathrm{H}1}(2)\cdot 1s_{\mathrm{H}2}(1)]\, d\tau_1\, d\tau_2 \\ &\equiv J_{12} \end{aligned} \tag{13.13}$$

as well as

$$\begin{aligned} &\int_6 [1s_{\mathrm{H}1}(2)\cdot 1s_{\mathrm{H}2}(1)]^*\frac{e^2}{4\pi\epsilon_0 r_{12}^2}[1s_{\mathrm{H}1}(1)\cdot 1s_{\mathrm{H}2}(2)]\, d\tau_1\, d\tau_2 \\ &= \int_6 [1s_{\mathrm{H}1}(2)\cdot 1s_{\mathrm{H}2}(1)]^*\frac{e^2}{4\pi\epsilon_0 r_{12}^2}[1s_{\mathrm{H}1}(1)\cdot 1s_{\mathrm{H}2}(2)]\, d\tau_1\, d\tau_2 \\ &\equiv K_{12} \end{aligned} \tag{13.14}$$

Equation 13.13 represents two electrons in defined atomic orbitals. The first electron is in H1's atomic orbital and the second electron is in H2's atomic orbital, or vice versa. Since the two hydrogen atoms are the same, the two integrals are equal to each other. The operator is the repulsion due to both electrons having the same, negative charge. Integrals of the form in equation 13.13 are called *Coulomb integrals* and are represented by the letter J. Since coulombic forces were known by classical mechanics, an integral involving such coulombic effects is not surprising for multielectron systems (indeed, they appeared in the helium atom).

However, equation 13.14 is something different. The coulombic repulsion between negatively charged electrons is still a part of the operator, but the wavefunctions are different. The integrals involve not only electron 1 on H1 and electron 2 on H2, but electron 1 *on H2* and electron 2 *on H1*. Since the integrand involves the electrons exchanging atoms, equation 13.14 is the general form for an *exchange integral*, denoted by *K*. *Exchange integrals do not have any classical counterpart*. It can be compared to a tug of war with two people on each side: if the tuggers both change sides, the game is unchanged, right? Classically, this is so, but quantum mechanically, it is different. The exchange integrals *K* affect the total energy of the molecule, even something as simple as H_2, and their existence represents one reason why classical mechanics couldn't adequately describe molecules. Classical mechanics completely missed the exchange integral contribution to the total energy of a molecular system.

Exchange integrals appear in all systems with more than one electron. Their contributions to the energy of the system cannot be ignored. In the case of an excited state of the helium atom having the electron configuration $1s^1\ 2s^1$, *K* is about 1/10 of the Coulomb integral *J*, indicating that it has a substantial effect on the predicted energy of the system.

Example 13.14

What are the expected valence bond wavefunctions for lithium hydride, LiH?

Solution

In an initial valence bond approximation, the $1s^2$ electrons of Li would be ignored, assuming that they don't participate in the bonding because they aren't in the valence shell. (Their presence is accounted for by assuming some constant amount of energy added to the entire diatomic system.) Therefore, we need to consider only the single 1*s* electron of H and the single 2*s* electron in the valence shell of Li. Of course, the proper spin functions must also be included. Analogous to the valence bond wavefunctions for H_2, those for LiH are

$$^1\Psi_{\text{LiH}} = \frac{1}{\sqrt{2}}[1s_{\text{H}}(1)\cdot 2s_{\text{Li}}(2) + 1s_{\text{H}}(2)\cdot 2s_{\text{Li}}(1)]\cdot\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

and

$$^3\Psi_{\text{LiH}} = \begin{cases} \dfrac{1}{\sqrt{2}}[1s_{\text{H}}(1)\cdot 2s_{\text{Li}}(2) - 1s_{\text{H}}(2)\cdot 2s_{\text{Li}}(1)]\cdot\alpha(1)\alpha(2) \\[2ex] \dfrac{1}{\sqrt{2}}[1s_{\text{H}}(1)\cdot 2s_{\text{Li}}(2) - 1s_{\text{H}}(2)\cdot 2s_{\text{Li}}(1)]\cdot\dfrac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \\[2ex] \dfrac{1}{\sqrt{2}}[1s_{\text{H}}(1)\cdot 2s_{\text{Li}}(2) - 1s_{\text{H}}(2)\cdot 2s_{\text{Li}}(1)]\cdot\beta(1)\beta(2) \end{cases}$$

(The spatial parts of the $^3\Psi_{\text{LiH}}$ wavefunctions are the same. Only the spin parts are different.) This example uses LiH because of the correspondence between its valence bonds and those of H_2, as it should be recognized that such expressions, though useful, can get very complicated very quickly when the number of valence electrons, and thus the number of valence bond wavefunctions, increases.

13.11 Hybrid Orbitals

The idea of valence orbitals itself does not use much symmetry, which is the main focus of this chapter. But the idea of hybrid orbitals does, and it also makes use of atomic orbitals of the valence-bonding sort. We will assume during this discussion that the bonding that occurs between atoms in a molecule exists between atomic orbitals in the valence shell only.

As an example, consider the methane molecule, CH_4. It consists of four hydrogens, each of which contributes a 1s valence orbital to the molecule, and a carbon atom, which in its valence shell has the 2s orbital and three 2p orbitals, which we represent as $2p_x$, $2p_y$, and $2p_z$ orbitals. The fact that carbon has only two 2p electrons in that subshell does not mean that there are only two 2p orbitals. The mathematics of quantum mechanics requires that p orbitals come in triplicate. Recall that these p orbitals can point in specific directions arbitrarily defined as the x-axis, the y-axis, and the z-axis. The three p orbitals are perpendicular to each other, 90° apart.

Methane is a covalent molecule known to have the shape of a tetrahedron, where the bonds make angles of 109.45° with the other bonds.* Figure 13.21 illustrates a potential problem: although the methane molecule has the shape of a tetrahedron, the valence orbitals of the carbon atom don't. How can methane have its shape? This question isn't confined to organic molecules. The water molecule is bent at 104.5° and NH_3 has 107° bond angles, not the 90° of the p orbitals.

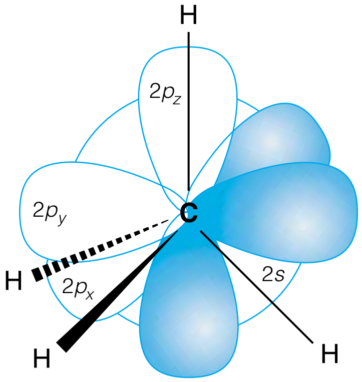

Figure 13.21 The atomic orbitals of carbon do not point in a tetrahedral direction. However, the methane molecule is known to be tetrahedral. The proper symmetry-adapted linear combinations of carbon's atomic orbitals do have tetrahedral symmetry.

In the 1930s, the development of valence bond theory (most notably by Linus Pauling) was extended to include linear combinations of the valence orbitals themselves. Such linear combinations are called *hybrid orbitals*. Specifically, the combination of a certain number of atomic orbitals provides linear combination hybrid orbitals that collectively have the proper symmetry. This single fact is what makes valence bond theory and hybrid orbitals such a useful interpretational tool in chemistry (whether or not such orbitals actually exist).

A crucial concept about hybrid orbitals is that the number of hybrid orbitals must equal the number of atomic orbitals that are combined. Thus, two atomic orbitals will combine to make two hybrid orbitals, four atomic orbitals will combine to make four hybrid orbitals, and so forth. Orbitals that do not combine to make hybrid orbitals continue to act as regular atomic orbitals.

As an example, consider the carbon atom in a methane molecule. The carbon atom is making four bonds to the surrounding hydrogen atoms. One s and three p orbitals make up the valence shell of the carbon atom. Instead of considering them individually, suppose we assume that they combine in linear combinations. With four atomic orbitals, we can define four independent linear combinations. The first, simplest such combination is

$$\eta_1 = c_1 s + c_2 p_x + c_3 p_y + c_4 p_z$$

where η is the lowercase Greek letter eta. As with any linear combinations, each wavefunction is multiplied by an expansion coefficient c_i ($i = 1$ to 4, in this case). The values of these constants need to be determined before the function is complete, so that η_1 is normalized. However, it can be shown that all of the constants are equal to $\frac{1}{2}$. Therefore,

$$\eta_1 = \tfrac{1}{2}(s + p_x + p_y + p_z)$$

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*In fact, the demonstration of that fact was a major milestone in the advancement of organic chemistry. The argument was first made by the French chemist Joseph Le Bel and the Dutch chemist Jacobus van't Hoff in 1874.

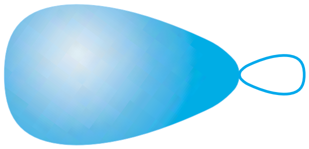


Figure 13.22 A single sp^3 orbital is reminiscent of a p orbital, but with unequal lobes. Like a p orbital, it does have one angular node.

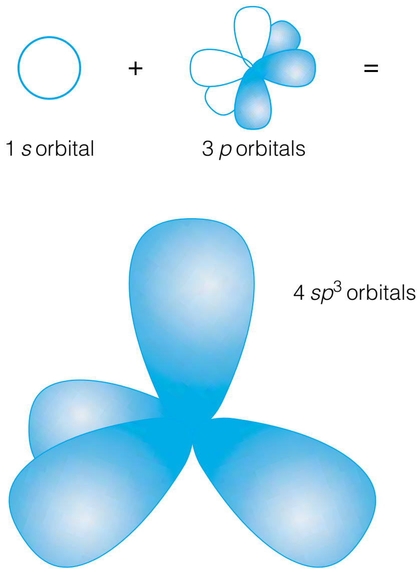


Figure 13.23 The four sp^3 orbitals, formed by the combination of the single s and the three p atomic orbitals, have tetrahedral symmetry. (For clarity, the small lobes of each orbital are not shown.) Their spatial geometry makes sp^3 orbitals very useful in explaining the structures of organic molecules.

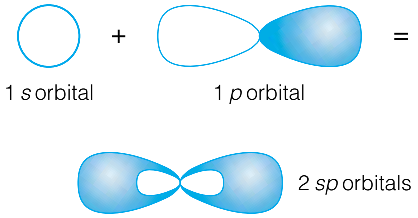


Figure 13.24 The two sp hybrid orbitals, formed by the combination of one s and one p atomic orbital, point in opposite directions. They are used to explain the linear geometries of molecules like BeH_2 and C_2H_2.

The wavefunction η_1 is a hybrid orbital, composed of one part s orbital and three parts p orbital. The other three hybrid orbitals are

$$\begin{aligned}\eta_2 &= \tfrac{1}{2}(s + p_x - p_y - p_z)\\ \eta_3 &= \tfrac{1}{2}(s - p_x - p_y + p_z)\\ \eta_4 &= \tfrac{1}{2}(s - p_x + p_y - p_z)\end{aligned} \tag{13.15}$$

(The numbering of the hybrid orbitals is arbitrary.) Because these hybrid orbitals are the combinations of one s orbital and 3 p orbitals, they are called sp^3 *hybrid orbitals.* These hybrid orbitals can be represented graphically just as hydrogen-like orbitals are. Figure 13.22 shows a cross-section of one orbital, which resembles a p orbital but has one enlarged lobe and one shrunken lobe. The plot of the four sp^3 orbitals in Figure 13.23 shows the spatial relationship of the four hybrid orbitals. The larger lobes of the four hybrid orbitals make the shape of a tetrahedron. When these four orbitals overlap with orbitals of another atom to make four bonds, the bonds made point in the direction of a tetrahedron. This accounts for the known tetrahedral shape of methane: the valence orbitals of the carbon atom can be thought of as not "pure" s and p orbitals, but sp^3 hybrid combinations that together have a tetrahedral shape.

In considering the hybrid orbitals in the valence shell of an atom, one must provide a hybrid orbital for each σ (sigma) bond (defined in the previous chapter as a bond having cylindrical electron density between the nuclei making the bond) the atom makes as well as nonbonding valence electron pairs. In the case of methane, in which the carbon atom makes four σ bonds, four hybrid orbitals are required: the four sp^3 hybrids made from the four atomic orbitals from the carbon valence shell.

Different atoms make different numbers of bonds, and also have nontetrahedral shapes. The covalent molecule BeH_2 is linear, with the two bonds made by the Be atom pointing in opposite directions. This sounds like one of the p orbitals, but the ground-state electron configuration of the Be valance shell is $2s^2$. No p orbitals are occupied. However, if the s orbital and one of the p orbitals combine,

$$\begin{aligned}\eta_1 &= \frac{1}{\sqrt{2}}(s + p_z)\\ \eta_1 &= \frac{1}{\sqrt{2}}(s - p_z)\end{aligned} \tag{13.16}$$

then the resulting two hybrid orbitals have relative directions as shown in Figure 13.24: they are oriented 180° from each other. These *sp hybrid orbitals* can make σ bonds with the hydrogen atoms, yielding a molecule that has a linear shape. The other two orbitals in Be, the p_x and the p_y, are unaffected by the hybridization and are unoccupied. (Using the p_z orbital in equations 13.16 was arbitrary.)

In cases where three hybrid orbitals are needed, a combination of the one s orbital and two of the p orbitals is assumed. The choice depends on how one defines the system. Assuming that one wants a hybrid orbital pointing along the z-axis, using the p_z orbital and (arbitrarily) the p_x orbital provides three sp^2 *hybrid orbitals* in the xz plane. They have the forms

$$\begin{aligned}\eta_1 &= \frac{1}{\sqrt{3}}s + \sqrt{\frac{2}{3}}p_z\\ \eta_2 &= \frac{1}{\sqrt{3}}s + \frac{1}{\sqrt{2}}p_x - \frac{1}{\sqrt{6}}p_z\\ \eta_3 &= \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{2}}p_x - \frac{1}{\sqrt{6}}p_z\end{aligned} \tag{13.17}$$

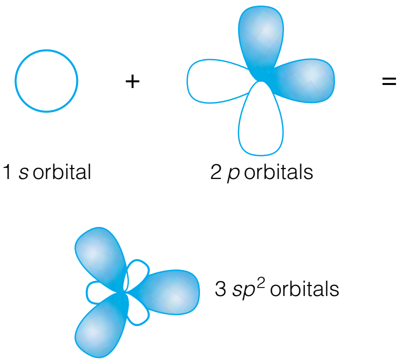


Figure 13.25 The three sp^2 hybrid orbitals are formed by the combination of one s and two p atomic orbitals. They are arranged in a plane and have the shape of an equilateral triangle. These hybrid orbitals are used to explain the trigonal planar structure of molecules like BF_3.

These three orbitals have the relative spatial orientation shown in Figure 13.25. They are all in the same plane and make 120° angles with each other. The molecule BF_3, where the boron atom makes three σ bonds to fluorine atoms, can be described as having sp^2 hybrid orbitals. The remaining p orbital retains its original, hydrogen-like form.

Example 13.15

Show that two of the sp^2 hybrid orbitals on the same atom are orthogonal.

Solution

Using η_2 and η_3 from equations 13.17 above, consider the following integral:

$$\int \left(\frac{1}{\sqrt{3}}s + \frac{1}{\sqrt{2}}p_x - \frac{1}{\sqrt{6}}p_z\right)^* \left(\frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{2}}p_x - \frac{1}{\sqrt{6}}p_z\right) d\tau$$

Since all of the atomic orbitals are real, the complex conjugate makes no change. The above expression can be expanded term by term into a sum of nine simpler integrals:

$$\begin{aligned}
&\int \frac{1}{\sqrt{3}}s \cdot \frac{1}{\sqrt{3}}s \, d\tau - \int \frac{1}{\sqrt{3}}s \cdot \frac{1}{\sqrt{2}}p_x \, d\tau - \int \frac{1}{\sqrt{3}}s \cdot \frac{1}{\sqrt{6}}p_z \, d\tau \\
&+ \int \frac{1}{\sqrt{2}}p_x \cdot \frac{1}{\sqrt{3}}s \, d\tau - \int \frac{1}{\sqrt{2}}p_x \cdot \frac{1}{\sqrt{2}}p_x \, d\tau - \int \frac{1}{\sqrt{2}}p_x \cdot \frac{1}{\sqrt{6}}p_z \, d\tau \\
&- \int \frac{1}{\sqrt{6}}p_z \cdot \frac{1}{\sqrt{3}}s \, d\tau + \int \frac{1}{\sqrt{6}}p_z \cdot \frac{1}{\sqrt{2}}p_x \, d\tau + \int \frac{1}{\sqrt{6}}p_z \cdot \frac{1}{\sqrt{6}}p_z \, d\tau
\end{aligned}$$

and the constants can be removed to outside the integral. For each resulting integral, those that have different atomic orbitals are identically zero (because atomic orbitals themselves are orthogonal). The only remaining nonzero integrals are

$$\tfrac{1}{3}\int s \cdot s \, d\tau - \tfrac{1}{2}\int p_x \cdot p_x \, d\tau + \tfrac{1}{6}\int p_z \cdot p_z \, d\tau$$

which, because the atomic orbitals are normalized, yields

$$\tfrac{1}{3} - \tfrac{1}{2} + \tfrac{1}{6} = 0$$

Since it can be shown that any combination of different hybrid orbitals yields exactly zero, the hybrid orbitals are in fact orthogonal.

For third-row elements and larger atoms, especially those in the p block, the existence of d orbitals introduces other possible hybridization schemes where the d orbitals themselves participate. The inclusion of one d orbital with the s and the three p orbitals yields five *sp^3d hybrid orbitals,* which collectively have an overall trigonal bipyramidal shape (like in PCl_5). The inclusion of two d orbitals with the s and p orbitals yields six sp^3d^2 hybrid orbitals, which collectively have an octahedral shape (like in SF_6).

These are the most common hybridization schemes, as well as the most ideal. Many real systems are described as having only partial hybrid character. For example, the H_2O molecule has a bond angle of 104.5°, not the 109.45° required by pure sp^3 hybrid orbitals. This is somewhat closer to the 90° angles of unhybridized p orbitals, suggesting more of a p orbital contribution to the hybrid orbital description of the O–H bonds. In fact, based solely on the bond angle, some equations (not given here) predict a hybrid orbital that is 81% p orbital and only 19% s orbital (as opposed to 75% p orbital and 25% s orbital for a pure sp^3 hybrid orbital). However, in most cases a "pure" hybrid orbital can be assumed and acts as a good enough approximation.

Hybridization and symmetry are intimately connected because of the relationships seen above: atomic centers in molecules that have certain hybridization have specific shape. Atoms that make *sp* hybrid orbitals impart a linear shape about that atomic center (which might suggest $C_{\infty v}$ or $D_{\infty h}$ point groups, for simple molecules). Atoms that have sp^2 hybrid orbitals make bonds in a threefold, or *trigonal,* shape. They also form planar molecules, since the three σ bonds formed by the sp^2 hybrid orbitals are in the same plane. Atoms having sp^3 hybrid orbitals have a tetrahedral molecular shape about that atom. Such a correspondence between molecular geometry and hybridization, though approximate, is a powerful tool in understanding the general shape of molecules.

In determining the irreducible representation labels for the hybrid orbitals, one must consider all hybrid orbitals as a set and how that set changes when the various classes of symmetry operations act on the set. If a hybrid orbital is moved onto itself, it contributes $+1$ to the character of that symmetry class. If a hybrid orbital is negated, it contributes -1 to the character. If a hybrid orbital is moved to the position of another hybrid orbital, then it contributes 0 (zero) to the character. Although many classes have more than one individual symmetry operation represented, all symmetry operations in a class have the same character (which is how we separated symmetry operations into classes previously). Therefore only one symmetry operation for each class needs to be considered, and the usual choice is the easiest symmetry operation to visualize. The contributions of all hybrid orbitals are summed up—not all of the hybrid orbitals will have the same contributions for any particular symmetry operation (except *E*, of course). This set of characters is compared to the irreducible representations of the point group. If necessary, the great orthogonality theorem is applied. This determines the labels for the hybrid orbitals. Since only orbitals of the same irreducible representation can interact to make molecules, such labels are indispensable when considering the fine points of atoms bonding to make molecules.

The following example illustrates this process.

Example 13.16

Determine the irreducible representations for sp^3 hybrid orbitals in the T_d point group.

Solution

Figure 13.26 shows the set of four sp^3 orbitals, labeled individually (although we recognize that we can't label them in reality). Collectively, they have tetrahedral or T_d symmetry. Each part of Figure 13.26 shows the effect of one symmetry operation from each of the five classes in the T_d point group. For *E*, Figure 13.26a shows that each hybrid orbital operates onto itself and so contributes + 1 to the total character; therefore, $\chi_E = 4$. Figure 13.26b shows that a C_3 operation keeps one orbital in place (which therefore contributes $+1$) and three others exchanging positions (which therefore contribute 0 each). Therefore, for the set of four orbitals, $\chi_{C_3} = 1$. Figure 13.26c shows that for C_2, all of the orbitals are operated onto different orbitals, so that $\chi_{C_2} = 0$. Figure 13.26d shows that the S_4 operation has the same effect as C_2: moving all orbitals to the positions of different orbitals. Therefore, $\chi_{S_4} = 0$. Finally, Figure 13.26e shows that a σ_d plane of symmetry reflects two orbitals onto themselves (for an overall contribution of $+2$) and reflects the two other or-

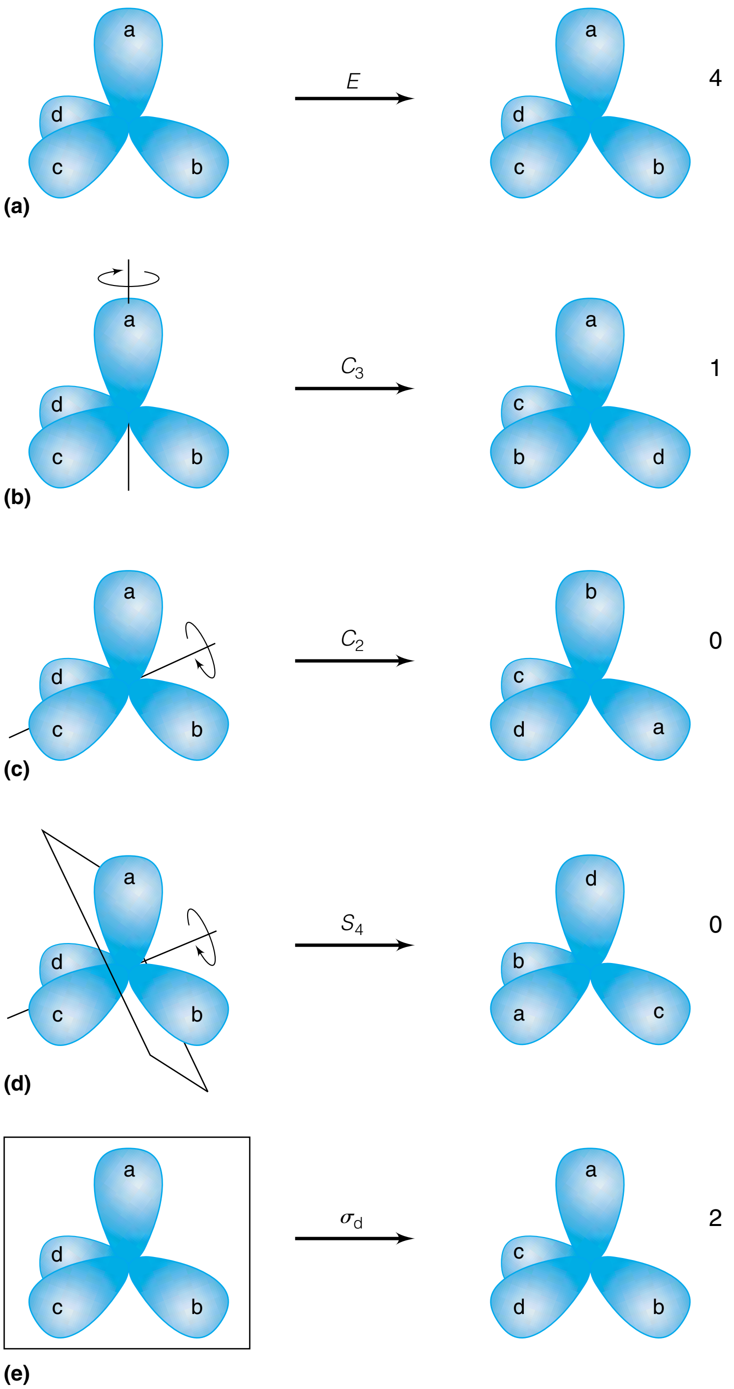


Figure 13.26 Operation of the symmetry classes of T_d on the sp^3 orbitals. The *a*, *b*, *c*, and *d* labels are used only to keep track of the individual hybrid orbitals. The number of hybrid orbitals that do not move when a symmetry operation occurs is listed in the final column. This set of numbers is the reducible representation Γ of the sp^3 orbitals. The great orthogonality theorem is used to reduce Γ into its irreducible representation labels.

bitals onto each other (for an overall contribution of 0). The total contribution to the character is 2, so that $\chi_{\sigma_d} = 2$. The complete set of characters is

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
sp^3	4	1	0	0	2

This is not one of the irreducible representations of T_d, so the great orthogonality theorem must be applied. Doing so shows that Γ above is a combination of A_1 and T_2, or rather,

$$\Gamma = A_1 \oplus T_2$$

Therefore, the four sp^3 hybrid orbitals can bond with any other molecular orbital or set of molecular orbitals that have either A_1 or T_2 irreducible representation labels in T_d symmetry.

The last statement of the above example mentioned a "set of orbitals." A similar procedure can be applied to a combination of atomic orbitals, just as the four sp^3 hybrid orbitals above were treated in combination. For example, in methane the four 1*s* atomic orbitals of hydrogen, which the symmetry operations in T_d move onto each other, represent such a set of orbitals. Perhaps not so surprisingly, the set of four 1*s* atomic orbitals can also be labeled as $A_1 \oplus T_2$ in the T_d point group.

13.12 Summary

Symmetry is a powerful and useful tool in chemistry. In this chapter, we have seen some examples of how symmetry ideas and group theory can be applied to quantum mechanics. Other topics involving symmetry will be introduced in future chapters. As illustrated in Example 13.12, symmetry considerations will be very important in our consideration of the spectroscopy of atoms and molecules. Symmetry will also be important when considering crystals and surfaces, topics covered near the end of the text. Any advanced study of chemistry must include symmetry and group theory, not only because it can be applied to wavefunctions, as we did here, but to the three-dimensional structures of all molecules.

EXERCISES FOR CHAPTER 13

13.1. In your own words, explain why an object that has more symmetry elements is said to have "higher symmetry" than an object with fewer symmetry elements.

13.2 & 13.3 Symmetry Operations and Point Groups

13.2. Identify the symmetry elements present in the following objects. **(a)** A blank sheet of paper, no holes. **(b)** A blank sheet of three-holed paper. **(c)** A baseball, including the stitching. **(d)** A round pencil, sharpened, with cylindrical eraser. **(e)** The Eiffel Tower. (You may have to look up a picture of it if you don't remember its shape!) **(f)** Any book. **(g)** A human body, approximately. (Don't consider internal organs, only outward appearance.) **(h)** A perfect starfish. **(i)** An unpainted stop sign.

13.3. Identify the point groups of the objects in the previous problem, where possible.

13.4. Show that $S_1 = \sigma$ and $S_2 = i$.

13.5. Without referring to Appendix 3, determine whether each of the following combinations of symmetry operations constitutes a complete group. For those that do not, supply the missing symmetry operation(s). **(a)** E, C_2 **(b)** E, σ_h **(c)** C_4, C_2, C_4^3 **(d)** E, C_3.

13.6. Any axis of symmetry C_n that rotates an object by $\theta = 360°/n$ about the z-axis can be generalized by the matrix

$$C_n = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \textbf{(13.18)}$$

(See Table 13.1.) Determine the matrix forms of the C_2, C_3, C_6, and C_1 rotation operators.

13.7. Use equation 13.18 in the above exercise to deduce the general form for **(a)** the S_n operation and **(b)** the i operation.

13.8. What are the number of classes and the order of the following point groups? **(a)** C_{2v} **(b)** D_{2h} **(c)** D_{6h} **(d)** S_4 **(e)** C_s **(f)** T_d **(g)** O **(h)** O_h **(i)** $R_h(3)$

13.9. **(a)** Show that the C_{3v} point group satisfies the closure property of a mathematical group. **(b)** Show that the C_{3v} point group satisfies the associative law by evaluating $\sigma_v(EC_3)$ and $(\sigma_v E)C_3$.

13.10. **(a)** In the T_d point group, an S_4^{-1} improper rotation is equivalent to what other improper rotation? **(b)** In the D_{6h} point group, the symmetry operation labeled C_2^{-1} is equivalent to what other symmetry operation?

13.11. Determine which single symmetry operation of the following point groups is equivalent to the given combination of multiple symmetry operations. **(a)** In C_{2v}, $C_2\sigma_v = ?$ **(b)** In C_{2h}, $iC_2 = ?$ **(c)** In D_{6h}, $C_6\sigma_h = ?$ **(d)** In D_{2d}, $C_2C_2' = ?$ **(e)** In O_h, $iS_4 = ?$

13.12. Group theory requires that symmetry operations satisfy the associative law.

(a) Do they satisfy the commutative law? That is, does a different order of the same symmetry operations always yield the same answer? Provide a specific example to support your answer.

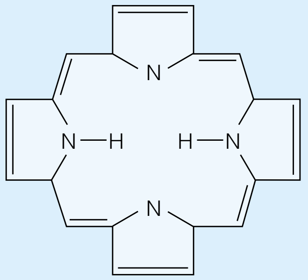


Figure 13.27 The structure of porphine. (See exercise 13.13.)

(b) In matrix algebra, matrix multiplication is not commutative. For any two given matrices A and B, it is not a certainty that $AB = BA$. Does this support or refute your conclusion in part a, and why?

13.13. Figure 13.27 shows the structure of the molecule porphine. Determine the symmetry elements present in the molecule, and its point group. Does the point group change if an Fe^{2+} ion is substituted for the two hydrogens in the center of the porphine ring?

13.14. In Example 13.3e, we are assuming that resonance structures of NO_3^- are "averaging" out the symmetry to an overall D_{3h} point group. If resonance weren't assumed, what point group would define the structure of NO_3^-?

13.15. Identify all the symmetry elements present in the tetrahedron, the cube, and the octahedron.

13.16. Point groups are called such because all of the symmetry elements in the group intersect in one point in space. For point groups that have i as a symmetry operation, why must i be at that point?

13.4 Molecules and Symmetry

13.17. Determine the point groups of the following molecules. **(a)** Hydrogen peroxide, H_2O_2 (It is *not* planar.) **(b)** Allene, $CH_2{=}C{=}CH_2$ **(c)** D-glycine (Its absolute stereochemistry can be found in any good organic or biochemistry textbook.) **(d)** L-glycine, and compare with part c above **(e)** *cis*-1,2-dichloroethylene **(f)** *trans*-1,2-dichloroethylene **(g)** Toluene, $C_6H_5CH_3$ **(h)** 1,3-Cyclohexadiene.

13.18. Determine the point groups of the following molecules. **(a)** Hydrogen selenide, H_2Se. **(b)** Partially deuterated hydrogen sulfide, or HDS **(c)** The chair conformer of cyclohexane, C_6H_{12} **(d)** The boat conformer of cyclohexane, C_6H_{12} **(e)** $Fe(CO)_5$, which has a trigonal bipyramidal structure **(f)** CO_3^{2-}, which has three resonance structures that contribute to its overall shape **(g)** The perfectly staggered conformer of ethane **(h)** The perfectly eclipsed conformer of ethane **(h)** 1,4-Cyclohexadiene

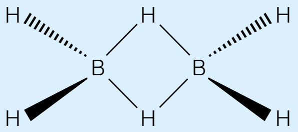
13.19. Identify the point group of the wavefunctions of the following molecules. **(a)** Deuterium oxide, D_2O (where $D = {}^2H$) **(b)** Boron trichloride, BCl_3 **(c)** Methylene chloride, CH_2Cl_2

13.20. Identify the point group of the wavefunctions of the following molecules. **(a)** Hydrogen chloride, HCl **(b)** Sulfur dioxide, SO_2 **(c)** Sulfur trioxide, SO_3

13.21. **(a)** What would be the formulas of possible molecules that have carbon atoms in the positions of the vertices of the five Platonic solids, in the cases where normal valence rules apply? (That is, C forms four and only four bonds. Any bonds not made to other C atoms can be used by hydrogen atoms.) (*Note:* Not all Platonic solids can be mimicked by carbon atoms bonding together, because one requires five bonds at each vertex.) **(b)** Verify that the two smallest molecules contain the various symmetry elements of their respective cubic point group. (Three of the possible hydrocarbons have actually been synthesized. Can you find them in the chemical literature?)

13.22. Determine if the following species have permanent dipole moments. **(a)** Dichloromethane, CH_2Cl_2 **(b)** Chlorobenzene, C_6H_5Cl **(c)** Ammonia, NH_3 **(d)** Carbon dioxide, CO_2 **(e)** The carbonate ion, CO_3^{2-} **(f)** The phosphate ion, PO_4^{3-} **(g)** Uranium hexafluoride, UF_6 **(h)** Bromine, Br_2 **(i)** Hydrogen deuteride, HD (D = ^{2}H)

13.23. Which of the following species will *not* have permanent dipole moments? **(a)** Hydrogen cyanide, HCN **(b)** Carbonyl sulfide, OCS **(c)** Phosphorus pentachloride, PCl_5 **(d)** Trimethylamine, $N(CH_3)_3$ **(e)** Boron trifluoride, BF_3 **(f)** Diborane, which has the following structure:



where the bridging hydrogens are perpendicular to the four terminal hydrogens, which are all coplanar **(g)** Methane, CH_4 **(h)** Chloromethane, CH_3Cl **(i)** Dichloromethane, CH_2Cl_2 **(j)** Trichloromethane (or chloroform), $CHCl_3$ **(k)** Carbon tetrachloride, CCl_4 **(l)** 2,2-Dimethylpropane, $CH_3C(CH_3)_2CH_3$ **(m)** Cubane (see 13.21 above)

13.24. **(a)** Unlike methane, bromochlorofluoromethane (CHBrClF) is chiral. Determine all symmetry elements that are present in CHBrClF and identify its point group. **(b)** If the fluorine in this molecule were substituted with a hydrogen, what is the point group for the new molecule? Is it chiral?

13.5 Character Tables

13.25. Write out explicitly the 12 × 12 matrices that specify the change in atomic coordinates of NH_3 upon operation of the *E* symmetry operation and any σ symmetry operation.

13.26. For NH_3, write out explicitly the three 12 × 12 matrices for all three planes of symmetry σ, σ′, and σ″. How are they similar, and how are they different?

13.27. Show that the irreducible representations of the D_2 point group satisfy the closure requirement.

13.28. Show that the irreducible representations of the D_{2d} point group satisfy the closure requirement. You will have to use the great orthogonality theorem to reduce one combination.

13.29. Show that any two of the irreducible representations of the following point groups are orthogonal to each other. **(a)** C_2 **(b)** C_{2v} **(c)** D_{2h} **(d)** O_h **(e)** T_d

13.30. Using the character tables in Appendix 3, can you determine which symmetry element must be present in order to have a two-dimensional irreducible representation (that is, one that can be labeled using *E* instead of *A* or *B*)?

13.31. Why is it unnecessary to consider whether an irreducible representation from C_{4h} is orthogonal to an irreducible representation of D_{6h}?

13.32. Explain why the characters for the proper and improper rotations are mathematical expressions instead of numbers for $C_{\infty v}$ and $D_{\infty h}$.

13.33. Use the expressions in $R_h(3)$ to determine the characters of the *f* orbitals in an octahedral (O_h) environment. For the set of seven *f* orbitals, the character of the identity symmetry operation is 7.

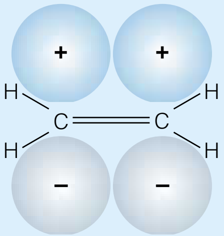
13.6 Wavefunctions and Symmetry

13.34. **(a)** What are the symmetry elements present in a plot of the function $F(\phi) = \sin\phi$? Assume that all symmetry elements intersect at the origin. **(b)** What are the symmetry elements present in a plot of the function $F(\phi) = \cos\phi$, again assuming that all elements intersect at the origin?

13.35. What are the symmetry elements present in a plot of the function $F(\phi) = \sin\phi$, assuming that the point of intersection for all symmetry elements is on the *x*-axis at $x = \pi/2$? (Another way of stating this is, What are the symmetry elements of the function *about the point* $x = \pi/2$?)

13.36. What point group(s) must the wavefunctions of all linear molecules belong?

13.37. The π bonds in the ethylene molecule can be represented like this:



where the two lobes are out of the plane made by the atoms. (In ground-state ethylene, only the bonding orbital is filled.) Determine the point group of ethylene and assign a symmetry species to the *p* bonds.

13.38. Consider the π bonds in ethylene shown in the previous exercise. In benzene (C_6H_6), six *p* orbitals from the six carbon atoms combine to make six molecular orbitals. In the lowest-energy π orbital, all of the phases assigned to the atomic *p* orbitals are the same on each side of the molecular plane; in the highest-energy π orbital, they alternate phases. Draw these two π orbitals and determine their symmetry species.

13.7 Great Orthogonality Theorem

13.39. Reduce the following reducible representations using the great orthogonality theorem.

(a) In the C_2 point group:

	E	C_2
Γ	5	1

(b) In the C_{3v} point group:

	E	$2C_2$	$3\sigma_v$
Γ	6	0	0

(c) In the D_4 point group:

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$
Γ	6	-2	2	2	-4

(d) In the T_d point group:

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ	7	-2	3	1	-1

13.40. Determine the resulting representations for the following products of irreducible representations.

(a) In C_{3v}, $A_1 \otimes A_2$

(b) In C_{6v}, $E_1 \otimes E_2$

(c) In D_{3h}, $A_2' \otimes A_1'' \otimes E''$

(d) In D_{6h}, $B_{2g} \otimes B_{2u}$

(e) In D_{6h}, $B_{1g} \otimes B_{1g}$

(f) In T_d, $E \otimes T_1$

(g) In T_d, $T_2 \otimes T_2$

(h) In O_h, $E_g \otimes T_{2g}$

13.8 Using Symmetry in Integrals

13.41. Assume that you are evaluating the integral of products of functions having symmetry labels in exercise 13.40, parts a–h. Which integrals, if any, are exactly zero due to symmetry considerations?

13.42. Assume that x-polarized light can be assigned an E symmetry species in a system that has C_{4v} symmetry. Can a transition from a Ψ_E state to a Ψ_{B_2} state occur? Why or why not?

13.43. Show that $s \rightarrow s$ transitions are not allowed in the hydrogen atom. To do this, show that the integral $\int \Psi_a(s)^* \widehat{O}\, \Psi_b(s)\, d\tau$ is exactly zero where $\widehat{O}$ is the operator representing the light. Assume that light has the symmetry species $D_u^{(1)}$ in this completely spherical system.

13.44. The five d orbitals in transition metals can be shown to have the following characters under tetrahedral (T_d) symmetry:

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ	5	-1	1	-1	1

(The character of E being 5 for the five d orbitals is not a coincidence!) In T_d symmetry, what symmetry species do the d orbitals have? What are the degeneracies of the symmetry species?

13.9 SALC-MO Theory

13.45. Construct the symmetry-adapted linear combination molecular orbitals for hydrogen sulfide, H_2S.

13.46. Referring to exercise 13.45: How would the symmetry-adapted linear combinations for the molecular orbitals of H_2S differ if the core atomic orbitals of S were included?

13.47. In Example 13.13, several of the molecular orbitals for H_2O were found to be simply atomic orbitals. Justify this in light of the idea that molecular orbitals are orbitals of the molecule as a whole, and not orbitals of the atoms.

13.48. Should the molecular orbitals for H_2O found in Example 13.13 be orthogonal? Will this always be the case?

13.49. How many SALCs can be constructed for CH_4 using all valence and core atomic orbitals?

13.10 & 13.11 VB Theory and Hybrid Orbitals

13.50. Construct a list comparing and contrasting VB theory with MO theory.

13.51. Why might one not be surprised to find that the first excited state of H_2 is represented by three very closely spaced lines in the spectrum?

13.52. Suppose you use p_0, p_{-1}, and p_{+1} along with s orbitals to construct hybrid orbitals. Will they be the same hybrid orbitals defined by the p_x, p_y, and p_z orbitals? Justify your answer.

13.53. Show that the individual sp orbitals, as written in equation 13.16, are orthogonal.

13.54. Show that the individual sp^3 orbitals, as written in equation 13.15, are orthogonal.

13.55. What is the rough hybridization of the carbon orbitals in the methyl carbonium ion, CH_3^+, which is almost perfectly planar triangular in shape?

13.56. Determine the symmetry species of the D_{3h} point group for the sp^2 hybrid orbitals, assuming that the C_3 axis is coincident with the z-axis and that one of the orbitals lies along the positive x-axis. (See example 13.16.)

13.57. Determine the D_{3h} symmetry species of the sp^3d hybrid orbitals, assuming that the C_3 axis is coincident with the z-axis and that one of the orbitals lies along the positive x-axis. (See Example 13.16.)

13.58. Determine the O_h symmetry species of the sp^3d^2 hybrid orbitals, assuming that the hybrid orbitals are all coincident with the Cartesian axes.

13.59. In propene (CH_3–$CH{=}CH_2$), the first carbon has sp^3 hybrid orbitals and the second carbon has sp^2 hybrid orbitals. These orbitals interact to make a σ bond. Why are these hybrid orbitals not orthogonal?

13.60. Using an appropriate software graphics package, input the forms of the *s* and *p* hydrogen-like wavefunctions (from Chapter 10), take the appropriate linear combinations of them, and verify the spatial orientation of *sp*, sp^2, and sp^3 hybrid orbitals. If you can find their forms in another reference, do the same thing for sp^3d and sp^3d^2 hybrid orbitals. You will need to use the *d* wavefunctions from Chapter 10, also.

13.61. Justify the fact that the nitrogen atom in ammonia is sp^3 hybridized even though it makes only three bonds to three hydrogen atoms.

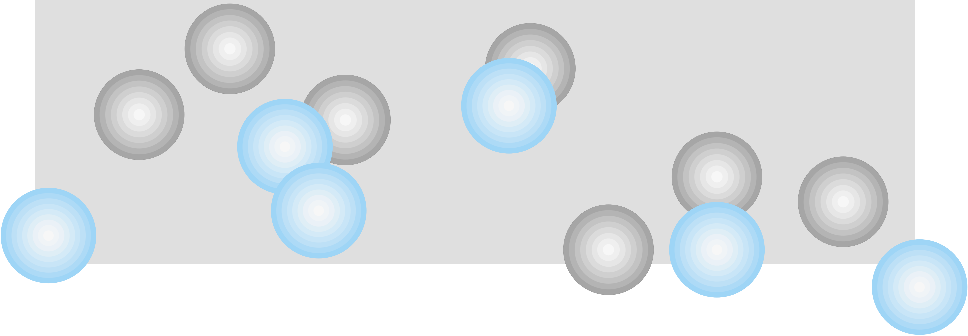
13.62. What symmetry species is assigned to the lone *p* orbital for a boron atom that is sp^2 hybridized?

Symbolic Math Exercises

13.63. Construct 90% probability surface diagrams for *sp*, sp^3, and sp^3 hybrid orbitals. Use $n = 2$ hydrogen-like wavefunctions as the bases for the hybrid orbitals.

14

Rotational and Vibrational Spectroscopy



VIRTUALLY EVERYTHING WE KNOW about matter comes from the interaction of matter with electromagnetic radiation. In its most straightforward fashion, such interactions define *spectroscopy.* Spectroscopy had its origin with Bunsen and Kirchhoff in the early 1860s, as recounted in Chapter 9. Spectroscopy was also an important factor in the development of quantum mechanics, as shown by the Rydberg equation for the spectrum of the hydrogen atom as well as Bohr's theory of hydrogen.

Spectroscopy probes energy levels of atoms and molecules. Therefore, it is an application of quantum mechanics. We have already seen that quantum mechanics provides exact answers for the energies of several ideal systems. What we will find is that many of these ideal systems are useful in understanding the spectroscopy—and therefore the energy levels—of atomic and molecular systems.

Atoms and molecules have energies due to several types of motion. In part, the Born-Oppenheimer approximation from Chapter 12 will be applied: we will treat various motions of atoms and molecules, and the energies of those motions, separately. Electronic, nuclear, rotational, and vibrational energy levels can and will be treated separately for the most part, although in some cases we will have types of spectroscopy that involve combinations of these energy levels.

Conveniently, the transitions that involve the different types of energy levels (electronic, vibrational, rotational) usually occur in different parts of the electromagnetic spectrum. This makes it even easier to consider them separately. We begin our multichapter treatment of spectroscopy by considering rotations and vibrations of molecules. Such motions are considered first for a reason. Both types of motions can be understood in terms of relatively simple quantum mechanics. We will also introduce some tools that we can apply to other forms of spectroscopy.

14.1 Synopsis

First, we explore the idea of selection rules, which are quantum-mechanical predictions for which energy levels of an atomic or molecular system will participate in a spectral transition. We will see that symmetry considerations are useful for predicting a transition from one energy level to another. Next, we discuss the electromagnetic spectrum and see how the different forms of spectroscopy relate to the energies of photons.

Rotational spectroscopy arises from the quantized rotations of molecules in three-dimensional space. Atoms do not have rotational spectra. However, diatomic molecules have a relatively simple rotational spectrum, since they can rotate in only two dimensions (a "rotation" about the internuclear axis will not be observed) and their behavior of rotation is the same for both directions. Nonlinear polyatomic molecules have one (for highly symmetric molecules) to three (for most, less-symmetric species) different rotations in space, complicating a rotational spectrum.

Vibrational spectroscopy arises from the vibrations of the individual atoms in molecules with respect to each other. The atoms are stretching, bending, or twisting about an imagined equilibrium position. Usually such motions occur at higher frequency than rotations, so vibrational spectra are observed using higher-energy light than in rotational spectroscopy. As with rotations, individual atoms do not have vibrational spectra, because two or more atoms bonded together are required for a vibration. Like rotations, vibrations occur in certain patterns. However, the symmetry of the molecules has a greater influence on the number of transitions observed in a vibrational spectrum. Transitions between vibrational energy levels also follow selection rules, which are different from those for rotations.

Spectroscopy is a powerful tool for studying matter. The treatment in this text cannot do the topic justice—series of books are written on just the topics in the next three chapters. However, the following material should give you some idea of how spectroscopy aids our understanding of atoms and molecules.

14.2 Selection Rules

In spectroscopy, an atomic or molecular system having a certain wavefunction and energy absorbs or emits energy, usually in the form of light, and in doing so becomes described by a different wavefunction and energy. In all forms of spectroscopy, it is the difference in energies of the wavefunctions that is the primary observable of interest. (Hence its overwhelming importance in quantum mechanics.) The law of conservation of energy requires that the light, usually in the form of a single photon, have the same energy as the difference in energy of the initial and final states. That is,

$$E(\Psi_{\text{final}}) - E(\Psi_{\text{initial}}) = E_{\text{photon}}$$

$$\Delta E = h\nu \qquad \textbf{(14.1)}$$

Equation 14.1 is written in the original form of the *Bohr frequency condition:* the difference in energy of the two quantum states equals the energy of the photon, which equals $h\nu$.

Remember, however, that wavefunctions have symmetry, and so do operators. The light that causes the system to go from one state to another (either by absorption or emission) can be assigned an irreducible representation from the point group of the system of interest. Quantum mechanics defines a specific expression, called a *transition moment,* to which the irreducible representations can be applied. For an absorption or emission of a photon, the transition moment M is defined as

$$M = \int \Psi^*_{\text{final}} \hat{\mu} \Psi_{\text{initial}}\, d\tau \qquad \textbf{(14.2)}$$

$$\hat{\mu} \equiv \hat{\mu}_x + \hat{\mu}_y + \hat{\mu}_z = \sum_{\substack{\#\text{ of}\\ \text{particles}}} e_i(x_i + y_i + z_i)$$

where $\hat{\mu}$ is the *electric dipole operator,* e is the charge on the particle, and x_i, y_i, and z_i are the coordinates of the particle. Transitions of this sort are *electric dipole transitions.* Transitions between wavefunctions can be prompted by other interactions (like magnetic dipole or polarization changes), but electric dipole transitions are the most common.

We can use the conclusions of the previous chapter on symmetry at this point. In order for the integral in equation 14.2 to have a nonzero numerical value, the irreducible representations of the three components of the integrand must contain the totally symmetric irreducible representation of the point group of the system, usually labeled A_1. That is,

$$\Gamma_{\Psi_{\text{final}}} \otimes \Gamma_{\hat{\mu}} \otimes \Gamma_{\Psi_{\text{initial}}} \subset A_1 \tag{14.3}$$

The great orthogonality theorem may be needed to determine the irreducible representations of the product in equation 14.3. If it contains A_1, then the integral may be nonzero and the transition between Ψ_{initial} and Ψ_{final}, caused by absorption or emission of electromagnetic radiation, is considered *allowed.* On the other hand, if the combination of irreducible representations in equation 14.3 does not contain A_1, then the integral defined in the transition moment must be identically zero and the transition cannot occur. It is a *forbidden transition.*

In reality, some forbidden transitions do occur, since the above definition does not take into account the nonideality of an atomic or molecular system. But forbidden transitions almost always have a much lower probability than do allowed transitions. This means that in spectral measurements, absorptions or emissions of radiation due to allowed transitions are typically stronger than for forbidden transitions. This fact is not only useful in understanding spectra but also reinforces the usefulness of the predictions of symmetry and quantum mechanics.

Although the above equations imply that a lot of symmetry analyses must be performed, that is not always the case. Equations 14.2 and 14.3 allow for the possibility of broad statements about which transitions will and will not be allowed for particular atomic or molecular systems. Such general statements, ultimately based on quantum-mechanics and symmetry, are called *selection rules.* Selection rules allow us to easily determine which transitions will occur. When one is faced with a spectrum to interpret, knowledge of the selection rules is an indispensable tool in deriving physical information from the spectrum. Rotational and vibrational spectroscopy, in this chapter, are simplified to a large extent thanks to selection rules.

14.3 The Electromagnetic Spectrum

Light can be represented by a wave, like the one shown in Figure 14.1. The wave has a characteristic frequency ν and a wavelength λ, and the two are related to the speed of light, represented by the letter c, by the equation

$$c = \lambda \cdot \nu \tag{14.4}$$

The speed of light in vacuum is constant at 2.9979×10^8 m/s. The speed of light in vacuum is a universal constant, like Planck's constant. All light, no matter what the frequency or wavelength, travels at this speed in vacuum. The wavelength has units of length, whereas the frequency has units of 1/s, or s^{-1}. Frequency is thought of as the number of waves of light passing a certain point per second.

Light travels at different speeds in different media (like air or water), but since gases are so dispersed the speed of light through air is usually treated as

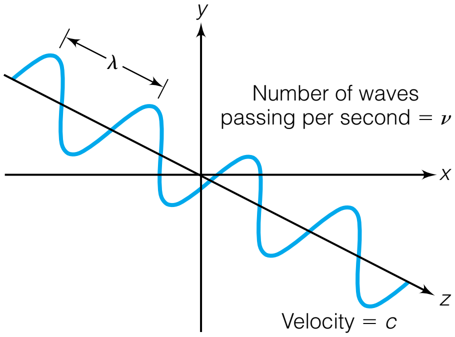


Figure 14.1 Light acts as a wave, with a wavelength λ and a frequency ν. In vacuum, all light has the same velocity, 2.9979×10^8 m/s. This value is given the symbol c.

Table 14.1 The electromagnetic spectrum[a]

Region	Frequency range (in s^{-1})	Wavelength range (variable units)	Energy range (kJ/mol of photons)
Gamma rays	$>3 \times 10^{17}$	<1 nm	$>120{,}000$
X rays	3×10^{17}–3×10^{16}	~1–10 nm	12,000,000–12,000
Ultraviolet (UV)[b]	7.5×10^{16}–7.5×10^{14}	4–400 nm	30,000–300
Visible light	7.5×10^{14}–3.9×10^{14}	400–770 nm	300–155
Infrared (IR)[c]	3.9×10^{14}–3×10^{11}	770 nm–1000 μm	155–0.12
Microwaves	3×10^{11}–3×10^{8}	1 mm–1000 mm	0.12–0.00012
Radio waves	$<3 \times 10^{8}$	>1000 mm	<0.00012

[a] Because the limits on the ranges are inexact, some of the boundaries may overlap.
[b] Occasionally separated into UVA (320–400 nm) and UVB (280–320 nm) regions.
[c] Occasionally separated into near IR (770–2500 nm), middle or mid-IR (2500–50,000 nm), and far IR (50,000 nm–1000 μm) regions.

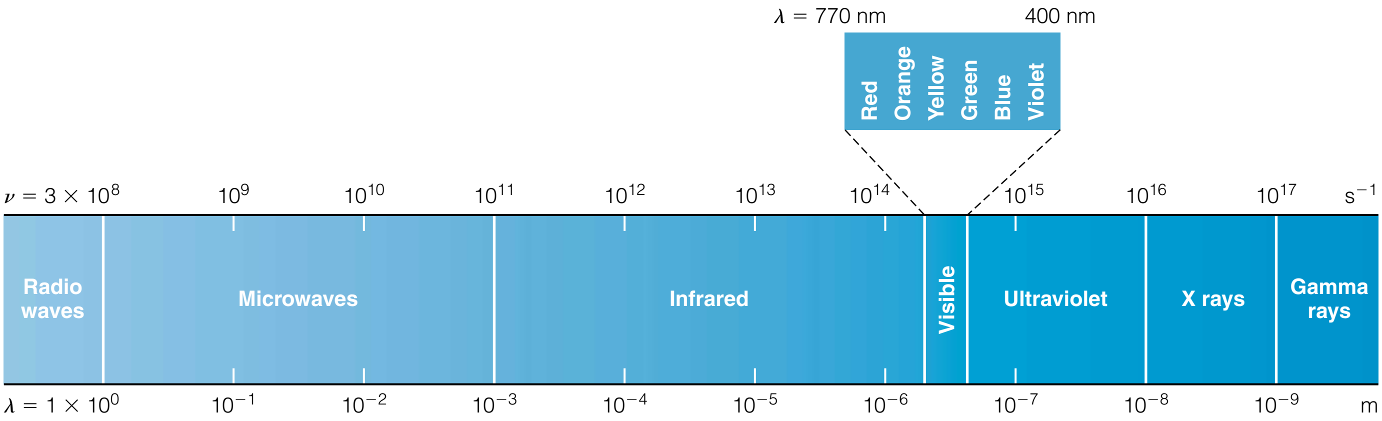
the same as in vacuum. This assumption is not valid for condensed phases like water, glass, or any other transparent medium.

The quantum theory of light, discussed in Chapter 9, provides a relationship between the energy of light and its frequency. Recall that light of a particular frequency ν comes in bundles of energy (which we call *photons*) having a certain, specific amount given by the formula

$$E = h\nu \tag{14.5}$$

Equations 14.4 and 14.5 allow us to convert between energy, wavelength, and frequency of light.

It is typical to divide the possible values of wavelength/frequency/energy of light into various regions. Table 14.1 lists the approximate frequencies, wavelengths, and energies of the regions, and Figure 14.2 shows a diagram of a continuous spectrum and how it is divided. Such divisions have historical as well as practical reasons. For example, one obvious division is *visible light,* which is light that we can see. Visible light is electromagnetic radiation having wavelengths from about 7700 Å to 4000 Å (or 7.700×10^{-7} m to 4.000×10^{-7} m). At higher frequencies (and therefore energies) than visible light is ultraviolet ("higher than violet," abbreviated UV) radiation, X rays, and gamma radiation.



(Region limits are approximate)

Figure 14.2 The electromagnetic spectrum. The top numbers are the approximate frequency boundaries of the regions, and the approximate wavelength boundaries are listed on the bottom. The visible portion of the spectrum, shown expanded, is actually a small part of the complete electromagnetic spectrum.

At lower frequencies than visible light, there are infrared ("lower than red," abbreviated IR) radiation, microwaves, and radio waves.

A convenience in spectroscopy is that most of the individual types of transitions (rotational, vibrational, electronic, and so on) occur in characteristic regions of the electromagnetic spectrum. Most pure rotational transitions occur by absorbing or emitting microwave radiation. Most pure vibrational transitions occur by absorbing or emitting infrared radiation. Similarly, electronic transitions occur in the presence of visible and ultraviolet light. There are exceptions, of course: transitions of electrons among the *f* orbitals (that is, in rare-earth atoms) can occur in the infrared region, and rotational transitions can be observed superimposed on a vibrational spectrum, also in the infrared region. But it is still convenient to refer to a type of spectroscopy by the region of the electromagnetic spectrum being probed.

Example 14.1

Assuming that the general regions of the various atomic or molecular transitions above are followed, put pure electronic, rotational, and vibrational transitions in order of increasing energy.

Solution

Assuming that electronic transitions occur in the visible or UV portion of the spectrum, the rotational in the microwave region, and the vibrational in the IR, then rotational transitions are lowest in energy, vibrational transitions are higher in energy, and electronic transitions are the highest of the three.

Another convenience for spectroscopists (but perhaps not for students!) is the fact that each type of spectroscopy uses its own units to indicate the energy changes measured by a spectrum. All units are related to energy, but one may have to apply $c = \lambda\nu$ or $E = h\nu$ to convert into energy units. Often, transitions in the microwave region are stated in units of frequency (MHz or GHz), whereas changes in electronic energies are typically expressed in units of nm or Å. In both cases, the numerical value and unit collectively refer to the photon that is absorbed or emitted in the course of the transition. Vibrational spectroscopy, in the infrared region, uses units of micrometers, or *microns,* to indicate the wavelength of the photon involved in the transition. (Microns are typically denoted μ instead of the SI-approved μm. Although the micron is not an SI-approved unit (micrometer is preferred), it is often found in scientific literature. Therefore, you should be familiar with it.) Commonly, the *wavenumber* unit is used. It is defined as the number of waves of light per centimeter, so it has the unit cm^{-1}.* It equals the reciprocal of the wavelength (in centimeters) of the light involved. Therefore,

$$\text{wavenumber} \equiv \tilde{\nu} = \frac{1}{\lambda} \qquad \textbf{(14.6)}$$

It is easy to show that the wavenumber of any photon is proportional to its frequency, so wavenumber is sometimes referred to as "frequency." Be careful to distinguish between $\tilde{\nu}$, having units of cm^{-1}, and ν (no tilde above the letter), which represents frequency and has units of s^{-1}.

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*The SI-approved unit for wavenumbers is m^{-1}, but cm^{-1} is used almost exclusively.

Example 14.2

Water absorbs infrared radiation that has a frequency of 1595 cm^{-1}. Convert this wavenumber into a wavelength in microns.

Solution

Rearranging equation 14.6 above, one finds

$$\lambda = \frac{1}{\tilde{\nu}}$$

Using the given wavenumber:

$$\lambda = \frac{1}{1595\ \text{cm}^{-1}} = 0.0006269\ \text{cm} = 6.269\ \text{microns} \quad \text{or} \quad 6.269\ \mu$$

Note how the centimeter unit comes to the numerator of the fraction.

14.4 Rotations in Molecules

Atoms are not considered candidates for rotation. An atom in free space probably rotates, but how would we be able to tell? At least two atoms, bonded together and tumbling in space, are necessary in order to consider rotation on a quantum-mechanical scale. The simplest molecule to consider is a diatomic gas. Its molecules rotate in space. The rotations are illustrated in Figure 14.3. Notice that there are only two ways the molecule can rotate, and the two rotations are the same except that the rotational axes are 90° apart. This system is very much like 3-D rotational motion. The energy levels for the pure rotational motions of a diatomic molecule are quantized and, to a very good approximation, given by the expression for the energy of a 3-D rigid rotor from Chapter 11:

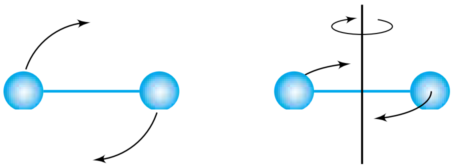

Figure 14.3 A diatomic (or polyatomic linear) molecule has only two defined rotational motions, which are equivalent to each other.

$$E_{\text{rot}} = \frac{J(J+1)\hbar^2}{2I} \qquad J = 0, 1, 2, \ldots \tag{14.7}$$

where E_{rot} is the rotational energy and I is the moment of inertia of the diatomic molecule, which is defined in terms of its *reduced mass* μ and the internuclear distance r:

$$I = \mu r^2$$

The molecule also has angular momentum, which you would expect it to have since it is rotating. The quantum number J is used to define the total angular momentum of the molecule rotating in three dimensions. The total angular momentum of a molecule is given by the same eigenvalue equation from three-dimensional rotational motion:

$$\hat{L}^2\Psi = J(J+1)\hbar^2\Psi \tag{14.8}$$

The square of the total angular momentum is the formally quantized observable. In order to get the magnitude of the angular momentum, you must take the square root of the eigenvalue from equation 14.8. There is also a z component of the total angular momentum for the diatomic molecule, and this z component is also quantized:

$$\hat{L}_z\Psi = M_J\hbar\Psi \qquad |M_J| \leq J \tag{14.9}$$

where now the quantum number for the molecule's z-component rotational motion is represented by M_J. M_J is bounded by J, just as m_ℓ was bound by ℓ. The total rotational energy of the molecule, equation 14.7, is determined only by J and not by M_J, the z component. Each rotational energy level is thus degenerate by a factor of $2J + 1$. Equations 14.8 and 14.9 are applicable not only to diatomic molecules but to all linear molecules. (For polyatomic linear molecules, however, the reduced mass is more difficult to calculate. We will not deal with such molecules here.)

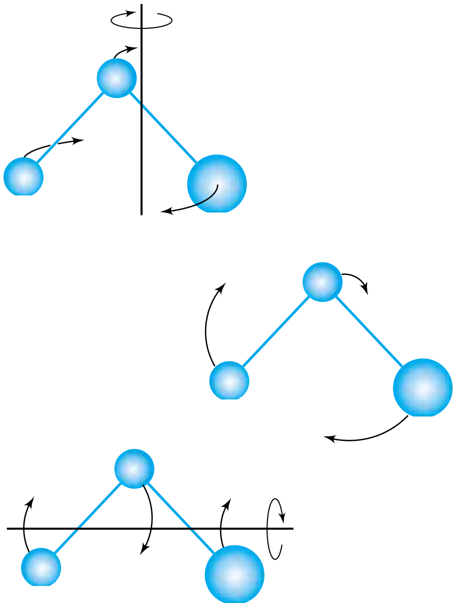

Figure 14.4 A nonlinear molecule has three different rotational motions. The symmetry of the molecule determines whether any or all of them are equivalent to each other.

Nonlinear molecules can rotate in *three* independent, mutually perpendicular directions, as illustrated in Figure 14.4. However, there is absolutely no guarantee that the rotation in one dimension is equivalent to rotations in the other two dimensions. For most molecules, all three rotations are different spatial motions. Also, the moment of inertia I for each dimension of each rotation is usually different. This makes the rotations of nonlinear molecules somewhat complicated. In general, there will be three different independent rotations, but even consideration of those can get substantially complicated. Generally, such asymmetric nonlinear molecules are treated using various levels of approximation to more symmetric systems, a sort of perturbation-theory kind of approach. We will not concern ourselves with such systems here.

Nonlinear molecules that have certain symmetry elements may, however, qualify for simpler treatment (leading, ultimately, to a better understanding of their properties). The key is the value of the moment of inertia of the molecule in the three perpendicular directions. One can always define a set of axes so that the *total* moment of inertia of the molecule can be described using three perpendicular components (one of which is exactly zero for linear molecules). These axes are called the *principal inertial axes,* or simply *principal axes,* of the molecule. One of the principal axes always lies coincident with the highest-order symmetry axis, if one exists. If all three moments of inertia are the same, then the molecule is called a *spherical top* and the rotational energy of the molecule is quantized and given by

$$E_{\text{rot, spherical}} = \frac{J(J + 1)\hbar^2}{2I} \tag{14.10}$$

This is the same expression used to define the energy levels of diatomic (or other linear) molecules. It can be shown that any molecule that has two or more noncoincident threefold or higher axes is a spherical top. Examples include methane (CH_4), sulfur hexafluoride (SF_6), and cubane (C_8H_8).

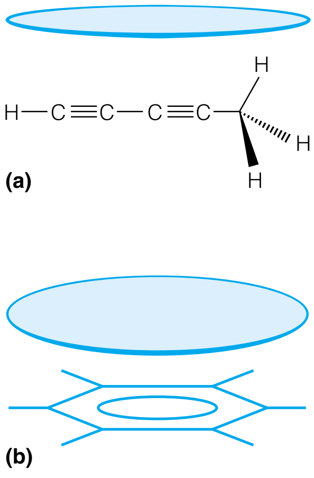

Figure 14.5 (a) A prolate symmetric top is long and cylindrical, like methyldiacetylene. (b) An oblate symmetric top is disk-shaped, like benzene.

If the molecule has three different moments of inertia, it is called an *asymmetric top.* The rotations of such molecules are complicated. As mentioned above, specific treatment is beyond the scope of this text, although this definition includes most molecules.

If a nonlinear molecule has a single threefold or higher axis, then it will have two of its three moments of inertia equal. Such molecules are called *symmetric tops.* There are two types of symmetric tops. If the two equal moments of inertia are lower than the unique moment of inertia, then the molecule is called an *oblate top.* If the two equal moments of inertia are higher than the unique moment of inertia, then the molecule is called a *prolate top.* Generally, oblate tops are flat and round, like a disk, and prolate tops are long and narrow, like a cigar. (See Figure 14.5.) Benzene (C_6H_6) is an oblate top, whereas ethane (CH_3CH_3) is a prolate top. The symmetry classification of many molecules is easy to do by inspection. However, in many cases, explicit calculation of the moments of inertia are necessary. NH_3 is one example since it is difficult to visualize all three of the principal axes. (Can you do it?) One axis is the molecular threefold rotational symmetry axis. The other two axes aren't so obvious. Calculation of the moments of inertia shows that ammonia is an oblate symmetric top.

Example 14.3

Classify the following molecules as linear or as spherical, prolate symmetric, oblate symmetric, or asymmetric tops. Drawing the structure of the molecules will help you visualize them.

a. Water, H_2O
b. The all-*trans* conformation of butane, C_4H_{10}
c. Chlorobenzene, C_6H_5Cl
d. Uranium hexafluoride, UF_6
e. Hydrogen cyanide, HCN
f. Carbonyl sulfide, OCS
g. The sulfate ion, $SO_4{}^{2-}$

Solution

a. Water has a single C_2 axis and so is an asymmetric top.
b. With its long carbon backbone, butane is a prolate top.
c. Chlorobenzene has C_{2v} symmetry and, like water, is an asymmetric top. Note how the substitution of one H in benzene with Cl changed the symmetry and, therefore, the rotational behavior of the molecule.
d. Uranium hexafluoride has several noncoincident C_4 axes, so it is a spherical top.
e. HCN is a linear molecule.
f. OCS is also a linear molecule.
g. $SO_4{}^{2-}$ is a tetrahedral ion, having several noncoincident C_3 rotational axes. Therefore it is a spherical top.

Example 14.4

From the general shape of the following molecules, define them as either prolate or oblate symmetric tops, or neither.

a. Tetrafluoroethylene, $CF_2{=}CF_2$
b. Boron trifluoride, BF_3
c. Trimethylamine, $N(CH_3)_3$
d. Dimethyldiacetylene, $CH_3{-}C{\equiv}C{-}C{\equiv}C{-}CH_3$

Solution

a. Though roughly a cigar-shaped molecule, tetrafluoroethylene does not have a threefold axis of symmetry. Therefore it is not a symmetric top.
b. The planar triangular boron trifluoride is an oblate symmetric top.
c. Borrowing from the statement above that ammonia, NH_3, is an oblate symmetric top, we might correctly assume that the trimethyl-substituted amine is also an oblate symmetric top.
d. The roughly linear molecule dimethyldiacetylene is a prolate symmetric top.

In considering the energy of rotation for symmetric tops, it is convenient to label the moments of inertia in order of magnitude, *lowest to highest,* using I_a,

I_b, and I_c (instead of I_x, I_y, and I_z). The definitions for the various types of nonlinear molecules are therefore

Spherical top: $I_a = I_b = I_c$

Oblate symmetric top: $I_a = I_b < I_c$

Prolate symmetric top: $I_a < I_b = I_c$

Asymmetric top: $I_a < I_b < I_c$

It also becomes convenient at this point to define the following rotational constants:

$$A = \frac{\hbar^2}{2I_a} \tag{14.11}$$

$$B = \frac{\hbar^2}{2I_b} \tag{14.12}$$

$$C = \frac{\hbar^2}{2I_c} \tag{14.13}$$

Example 14.5

Assuming standard SI units, what is the unit on the rotational constants *A*, *B*, or *C*?

Solution

Using just the units for the variables, which are J · s for Planck's constant and kg·m^2 for the moment of inertia, we have

$$\frac{(\text{J}\cdot\text{s})^2}{\text{kg}\cdot\text{m}^2} = \frac{\left(\frac{\text{kg}\cdot\text{m}^2}{\text{s}^2}\right)^2 \cdot \text{s}^2}{\text{kg}\cdot\text{m}^2} = \frac{\text{kg}\cdot\text{m}^2}{\text{s}^2} = \text{J}$$

You should satisfy yourself that the reduction of units from the second step to the third, which is the crucial one, is indeed valid.

Wavenumbers are commonly used as units to express the positions of rotational transitions. If expressions in terms of cm^{-1} are desired, equations 14.11–14.13 can be written as

$$A = \frac{\hbar^2}{2 \cdot I_a hc} = \frac{h}{8\pi^2 I_a c}$$

$$B = \frac{\hbar^2}{2 \cdot I_b hc} = \frac{h}{8\pi^2 I_b c}$$

$$C = \frac{\hbar^2}{2 \cdot I_c hc} = \frac{h}{8\pi^2 I_c c}$$

where *c* is the speed of light in units of *centimeters* per second.

The rotational energy of the molecules can then be expressed in terms of *A*, *B*, and *C* as well as the rotational quantum number. For spherical tops and linear molecules:

$$E_{\text{rot}} = BJ(J + 1) \tag{14.14}$$

where we have used the rotational constant *B* as the only necessary constant.

The rotational energies of symmetric tops are further divided into prolate and oblate symmetric tops. We first look at the prolate symmetric top, which has $I_a < I_b = I_c$. There is a *total angular momentum quantum number J* that determines the quantized *total* angular momentum:

$$\text{total angular momentum} = \sqrt{J(J+1)}\hbar$$

There is an additional quantized value. Recognize that a molecule that is not spherically symmetric can rotate three different ways. However, symmetric tops have one unique rotation and two equivalent rotations. The unique axis is called the *figure axis* for the molecule. It turns out that the component of the total angular momentum in the figure axis is also quantized. Since the definition of the figure axis depends on the molecule (it is molecule dependent), it can be considered a sort of molecule-defined z-axis. (This is different from an absolute, *spatially* defined z-axis.) The letter K is used to indicate the quantized *figure-axis component of the total angular momentum,* which follows the same rules as z-component angular momentum:

$$\hat{L}_z\Psi_{\text{mol}} = K\hbar\Psi_{\text{mol}} \qquad K = 0, \pm1, \pm2, \ldots \pm J \tag{14.15}$$

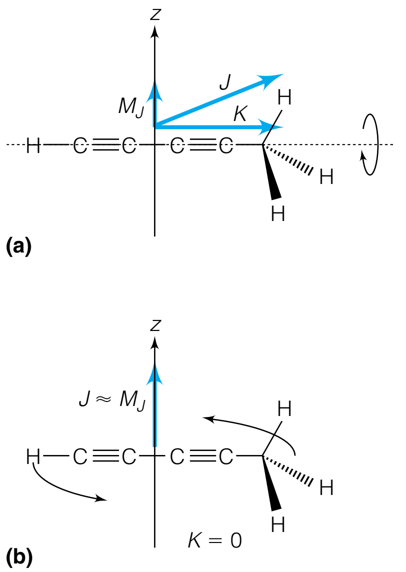

Figure 14.6 J represents the total angular momentum of the molecule. M_J is the z component of J. This z-axis can have any direction, but the figure axis depends on the structure of the molecule itself. (a) A rotation about the figure axis, which means the angular momentum quantum number K has a large value. (b) A rotation out of the figure axis, which means K equals 0 even though M_J is nonzero. In both cases, the value of J is the same.

Note that K is *bounded* by J (just like m_ℓ is bounded by ℓ). Figure 14.6 shows the differences in the definitions of the figure-axis component and the z component of the angular momentum. Angular momenta about both axes are quantized in symmetric top molecules. Equations 14.9 and 14.15 are both applicable to the rotations of symmetric top molecules.

It can be shown (we omit the detailed derivation here) that the total rotational energy of a prolate symmetric top is *quantized.* That energy, in terms of the quantum number J for the total angular momentum *and* the quantum number K for the figure-axis component of angular momentum, has the following expression:

$$E_{\text{rot}} = BJ(J+1) + (A-B)K^2 \tag{14.16}$$

In this case, the energy of the rotating molecule depends on *two* quantum numbers. Just as for linear molecules or the original 3-D rigid rotor, the energy is not dependent on the z component of the angular momentum. It *is* dependent on the figure-axis component. Because A is always greater than B, the second term in K is always positive (K^2 is always nonnegative) and represents an increase in the energy of the rotating molecule relative to a diatomic or spherical top molecule.

For an oblate symmetric top, a very similar expression for the quantized energy of rotation is obtained, except that now the lower two moments of inertia are equal and the largest is the unique one. But a similar derivation (again, omitted here) leads to a similar expression:

$$E_{\text{rot}} = BJ(J+1) + (C-B)K^2 \tag{14.17}$$

In this case, since C is always less than B, the second term in equation 14.17 will always be negative, so the second term contributes to an overall *decrease* in the rotational energy of the oblate molecule relative to a diatomic or spherical top molecule.

Example 14.6

Ammonia has two defined inertial moments: $I = 4.413 \times 10^{-47}$ kg·m^2 and $I = 2.806 \times 10^{-47}$ kg·m^2.

a. Label these as I_a, I_b, and I_c.

b. Calculate the rotational constants A, B, and C.
c. What is the value of the lowest nonzero rotational energy?
d. What is the value of the next lowest nonzero rotational energy?

Solution

a. Ammonia is an oblate symmetric top, having $I_a = I_b < I_c$. Therefore, the higher of the two defined inertial moments is the unique one: $I_c = 4.413 \times 10^{-47}\ \text{kg·m}^2$. The lower of the inertial moments is both I_a and I_b: $I_a = I_b = 2.806 \times 10^{-47}\ \text{kg·m}^2$.

b. From equations 14.11–14.13 above (and recognizing that since $I_a = I_b$, then $A = B$):

$$A = B = \frac{\hbar^2}{2I_a} = \frac{(6.626 \times 10^{-34}\ \text{J·s})^2}{(2\pi)^2 \cdot 2 \cdot 2.806 \times 10^{-47}\ \text{kg·m}^2} = 1.982 \times 10^{-22}\ \text{J}$$

$$C = \frac{\hbar^2}{2I_c} = \frac{(6.626 \times 10^{-34}\ \text{J·s})^2}{(2\pi)^2 \cdot 2 \cdot 4.413 \times 10^{-47}\ \text{kg·m}^2} = 1.260 \times 10^{-22}\ \text{J}$$

c. The lowest nonzero value of the rotational energy has $J = 1$ and $K = 1$ for an oblate top. Therefore, from equation 14.17:

$$E_{\text{rot}} = BJ(J + 1) + (C - B)K^2$$
$$= 1.982 \times 10^{-22}\ \text{J} \cdot 1(1 + 1) + (1.260 \times 10^{-22}\ \text{J} - 1.982 \times 10^{-22}\ \text{J})1^2$$
$$E_{\text{lowest}} = 3.242 \times 10^{-22}\ \text{J}$$

d. The next lowest rotational energy level has the same value for J, but $K = 0$. Substituting these quantum numbers into a similar expression, one gets

$$E_{\text{next lowest}} = 1.982 \times 10^{-22}\ \text{J} \cdot 1(1 + 1) + (1.260 \times 10^{-22}\ \text{J} - 1.982 \times 10^{-22}\ \text{J})0^2$$

The second term is zero, making the total energy dependent on only the first term of the expression:

$$E_{\text{next lowest}} = 3.964 \times 10^{-22}\ \text{J}$$

It is perhaps counterintuitive that a higher quantum number leads to a lower quantized energy.

14.5 Selection Rules for Rotational Spectroscopy

Given an understanding of the energy levels of molecules due to various types of motions, it is a simple step to consider the spectroscopy involving those motions, because spectroscopy involves a transition from one energy level to another. Spectroscopy uses the Bohr frequency condition, originally proposed by Neils Bohr in his theory of the hydrogen atom. This was discussed in section 14.2. Since the energy levels of rotations for simple molecules are known from the treatment above, determining the change in the energy levels is straightforward.

Classically, light is an oscillating electromagnetic field that will interact with other oscillating electromagnetic fields, much the same as two magnets or electrical charges will interact with each other. Consider a molecule whose only motion is rotation so that we can consider a "pure" transition involving only rotational quantum levels. Such a rotating molecule does not provide an oscillating electromagnetic field unless the molecule has a permanent dipole moment. If it does, the rotation will provide an oscillating electromagnetic field on the order of the light's oscillating field, and then the light and the molecule will interact. Figure 14.7 illustrates this interaction. In order to observe absorption or emission of light due to pure rotational transitions, the molecule *must* have a permanent dipole moment. (The phrase "pure rotational transitions" is crucial, since the several types of motions of a molecule can interact—"mix"—and seemingly violate such simple statements. We will consider some examples later.) The presence of a permanent dipole moment is sometimes referred to as a *gross selection rule,* since it relies on a general property of a molecule rather than a specific wavefunction of the molecule. More specific selection rules, based on wavefunctions, will be considered shortly.

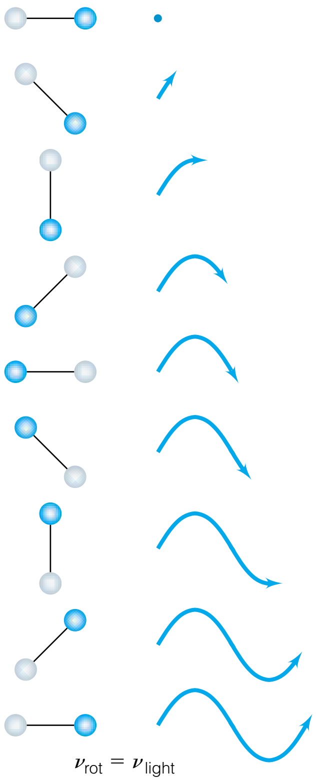

Figure 14.7 This series of drawings shows how the frequency of light and the frequency of rotational motion are equal if light is to be absorbed.

Example 14.7

Which of the following molecules will absorb or emit light due to rotational energy transitions?

a. Methane, CH_4
b. Hydrogen chloride, HCl
c. Water, H_2O
d. Carbon dioxide, CO_2
e. Acetylene, C_2H_2
f. Hydrogen cyanide, HCN
g. Benzene, C_6H_6

Solution

a. Methane has no permanent dipole moment; therefore it will not show pure rotational energy transitions.
b. HCl has a permanent dipole moment and so will exhibit pure rotational energy transitions.
c. H_2O will.
d. CO_2 will not.
e. C_2H_2 will not.
f. HCN will.
g. C_6H_6 will not.

This gross selection rule is general and considers a general property of the molecule. What about specific transitions between rotational quantum levels? Can any two rotational wavefunctions be involved in a transition, or is there a restriction on what wavefunctions can interact via absorption or emission of a photon? There is indeed a restriction, and it has to do with the fact that a photon has angular momentum. (This was alluded to in Chapter 9 when discussing Arthur Compton's experiments with X rays and their frequency change upon interaction with atoms.) Photons have one unit of angular momentum (they have $s = 1$), and so the law of conservation of angular momentum requires that the total angular momentum of an initial state (molecule + photon) must equal the total angular momentum of the final state (the molecule after it has absorbed or emitted the photon). The law of conservation of angular momentum thus requires that the absorption or emission of a photon must be accompanied by the change of the J quantum number by 1, either an increase of 1 (for absorption) or a decrease of 1 (for emission). One can write the following quantum-mechanical selection rule for rotational transitions:

$$\Delta J = \pm 1 \qquad \textbf{(14.18)}$$

where ΔJ refers to the change in the J quantum number for the rotational transition.* This is for an ideal process. Under real conditions, this selection rule is not strictly adhered to, but variances from equation 14.18 are rare and such transitions are only weakly absorbing or emitting (and so practically unnoticeable). Equation 14.18 therefore defines *allowed* rotational transitions. Other transitions where ΔJ is different from ± 1 are *forbidden.*

Linear molecules also have the z component of their total angular momentum quantized, and if the total angular momentum is changing by 1 unit, then that unit may be in the z-axis. But then again, it may not, so the M_J quantum number might either stay the same or change by 1 unit. Therefore, the selection rule for M_J is written

$$\Delta M_J = 0, \pm 1 \text{ for linear molecules} \tag{14.19}$$

We have already seen that symmetric top molecules have a second quantum number, K, used to define the quantized figure-axis component of the angular momentum. Interaction of the light field with the molecule's dipole, which must lie on the figure axis, is such that the electromagnetic field cannot change the molecule's rotation with respect to the figure axis. Therefore, the quantum number K is used to define the selection rule

$$\Delta K = 0 \tag{14.20}$$

14.6 Rotational Spectroscopy

Now that the selection rules have been established, the energies of transition can be determined. We want to determine ΔE, the change in energy between two rotational states involved in a transition. For now, we will express ΔE in terms of units of energy (usually J).

For a diatomic or linear molecule, ΔE in a rotational transition is the difference in energy of two adjacent states. For absorption, the transition can be labeled as $E(J) \rightarrow E(J+1)$, and the difference in energy is given by the difference between final and initial states:

$$\begin{aligned}\Delta E_{E(J)\rightarrow E(J+1)} &= E(J+1) - E(J)\\ &= \frac{(J+1)(J+1+1)\hbar^2}{2I} - \frac{(J)(J+1)\hbar^2}{2I}\\ \Delta E_{E(J)\rightarrow E(J+1)} &= \frac{(2J+2)\hbar^2}{2I} = \frac{(J+1)\hbar^2}{I}\end{aligned} \tag{14.21}$$

In an equation such as this that contains a quantum number, it is important to remember which state the quantum number J stands for. In this case, we are considering absorption, and J stands for the quantum number of the *lower*-energy state. To be consistent in this definition of J, for emission the transition will be written as $E(J+1) \rightarrow E(J)$, and the energy difference will have the same magnitude but with a negative sign, indicating that energy is lost. J still represents the quantum number of the lower-energy state. It is typical to use equation 14.21 for absorption *and* emission spectroscopy, and just keep track of whether light is absorbed or emitted.

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*In some circumstances, such as in odd-electron molecules like NO, $\Delta J = 0$ is allowed, but we will not consider these here.

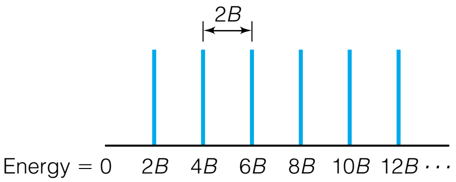


Figure 14.8 A pure rotational spectrum, displayed in units directly proportional to energy, shows a series of equally spaced lines. The energy separation between the lines equals $2B$.

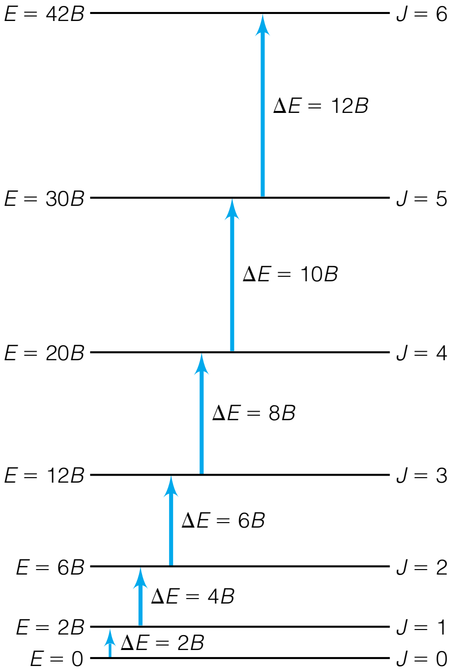


Figure 14.9 An energy-level diagram for the rotational motion of a diatomic molecule shows the allowed transitions and their energies.

Equation 14.21 is commonly rewritten in terms of the rotational constant B. Factoring out 2 from the terms involving J, equation 14.21 can be rewritten as

$$\Delta E = 2B(J + 1) \tag{14.22}$$

For absorption spectroscopy, the minimum J value is $J = 0$, so by considering the specific values of ΔE versus the value of J:

$$\begin{aligned}
\Delta E_{0\rightarrow 1} &= 2B(0 + 1) = 2B \\
\Delta E_{1\rightarrow 2} &= 2B(1 + 1) = 4B \\
\Delta E_{2\rightarrow 3} &= 2B(2 + 1) = 6B \\
\Delta E_{3\rightarrow 4} &= 2B(3 + 1) = 8B \\
\Delta E_{4\rightarrow 5} &= 2B(4 + 1) = 10B \\
&\vdots
\end{aligned}$$

Figure 14.8 shows a graphical representation of a typical rotational spectrum for a linear molecule. Figure 14.9 shows a diagram of the energy levels, and the allowed transitions are labeled. Compare the two figures, and you should be able to find the specific transition in Figure 14.9 that corresponds to the line in Figure 14.8. As suggested by the above equations, the spectrum consists of a series of equally spaced lines, spaced by an amount equal to $2B$. The spectrum will be a series of equally spaced lines only if the unit of display is directly proportional to energy, like frequency or wavenumber. If the spectrum were displayed in terms of a quantity inversely proportional to energy (like wavelength), then the lines of the spectrum would not be equally spaced. This illustrates the necessity of understanding the unit used to display a spectrum.

The above equations show something else about the rotational spectrum: its relationship to B, which in turn is related to the moment of inertia. For diatomic molecules, the moment of inertia I is defined simply as μr^2, where μ is the reduced mass and r is the internuclear separation of the two atoms. Rotational spectroscopy is therefore useful in calculating the sizes of diatomic molecules. This is a general capability of rotational spectroscopy, but it is most easily illustrated for diatomic molecules.

Example 14.8

Some of the lines in the rotational spectrum of HCl appear at 83.03, 104.1, 124.3, 145.0, and 165.5 cm^{-1}. The first line is the $J = 3 \rightarrow J = 4$ transition, so it equals $8B$. Determine the average value for B from this data and calculate the length of the HCl bond (which gives a good idea of the size of the molecule). Assume that these data are for ^{1}H and ^{35}Cl. You will have to convert the units of B from cm^{-1} to J in order for the units to work properly.

Solution

It is easy to see that the spacing between the lines is on the order of 21 cm^{-1}. Since the first line is the $J = 3 \rightarrow J = 4$ transition, we can make the following assignments:

$J = 3 \rightarrow J = 4$: line position $= 8B = 83.03\ \text{cm}^{-1}$, therefore $B = 10.38\ \text{cm}^{-1}$

$J = 4 \rightarrow J = 5$: line position $= 10B = 104.1\ \text{cm}^{-1}$, therefore $B = 10.41\ \text{cm}^{-1}$

$J = 5 \rightarrow J = 6$: line position $= 12B = 124.3\ \text{cm}^{-1}$, therefore $B = 10.36\ \text{cm}^{-1}$

$J = 6 \rightarrow J = 7$: line position $= 14B = 145.0\ \text{cm}^{-1}$, therefore $B = 10.36\ \text{cm}^{-1}$

$J = 7 \rightarrow J = 8$: line position $= 16B = 165.5\ \text{cm}^{-1}$, therefore $B = 10.34\ \text{cm}^{-1}$

The average value for B from this data is $10.37\ \text{cm}^{-1}$. The reciprocal of this gives an appropriate equivalent wavelength in centimeters, which is 0.09643 cm, or 9.643×10^{-4} m. Using $c = \lambda\nu$, this converts into a frequency of $\nu = 3.109 \times 10^{11}\ \text{s}^{-1}$, and using the equation $E = h\nu$, this converts to an energy of 2.060×10^{-22} J. (You should satisfy yourself on the reasons for all these steps in the conversion to joules.) Since the energy unit is joules, which is defined in terms of kg, the reduced mass of the $^1\text{H}^{35}\text{Cl}$ atom must be expressed in units of kg. The H atom has a mass of 1.66×10^{-27} kg, and the Cl atom has a mass of 5.81×10^{-26} kg. The reduced mass is therefore 1.61×10^{-27} kg. The only unknown in the expression

$$B = \frac{\hbar^2}{2\mu r^2}$$

is the distance r. Substituting for the known values (and not forgetting the 2π part of $\hbar$):

$$2.060 \times 10^{-22}\ \text{J} = \frac{(6.626 \times 10^{-34}\ \text{J·s})^2}{(2\pi)^2 \cdot 2(1.61 \times 10^{-27}\ \text{kg})r^2}$$

Rearranging and solving for the radius r:

$$r = 1.29 \times 10^{-10}\ \text{m} = 1.29\ \text{Å}$$

This is how rotational spectroscopy gives us an idea about the actual sizes of molecules.

Example 14.9

NO has a bond length of 1.151 Å. Predict where the first four lines of the pure rotational spectrum of NO will appear, in units of GHz. Refer to Example 14.8 for calculational details.

Solution

The reduced mass of NO is calculated to be 1.24×10^{-26} kg. We can calculate a value of B:

$$B = \frac{(6.626 \times 10^{-34}\ \text{J·s})^2}{(2\pi)^2 \cdot 2(1.24 \times 10^{-26}\ \text{kg})(1.151 \times 10^{-10}\ \text{m})^2}$$

where we have used the definition $1\ \text{Å} = 10^{-10}$ m to get all the units consistent with each other. We get

$$B = 6.77 \times 10^{-23}\ \text{J}$$

In units of frequency, we need to use $E = h\nu$ to get $\nu = 1.02 \times 10^{11}\ \text{s}^{-1}$. Since this can be written as $102 \times 10^{9}\ \text{s}^{-1}$, and since a GHz is 10^9 Hz, this corresponds to a value of 102 GHz. The first four lines, appearing at $2B$, $4B$, $6B$, and $8B$, are therefore found at 204, 408, 612, and 816 GHz.

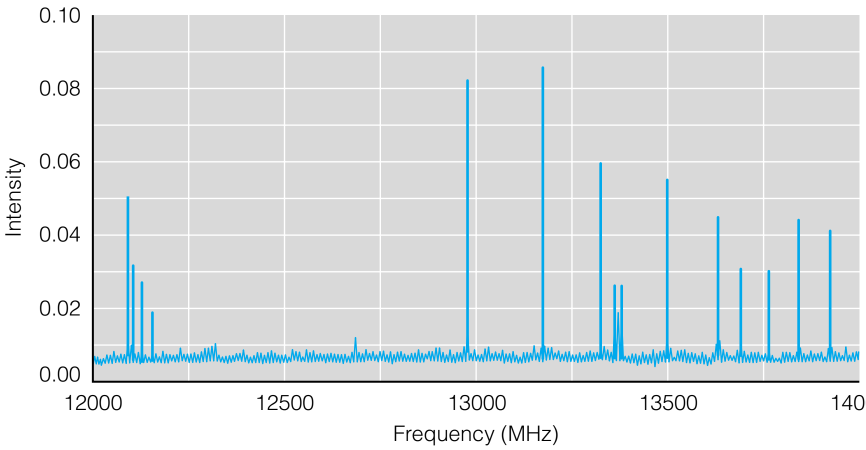


Figure 14.10 A pure rotational spectrum of sarin (a nerve gas), in units of frequency. Studies like this are useful in the development of detectors for nerve gas.

Pure rotational spectra usually occur in the microwave region of the electromagnetic spectrum, so the phrases "rotational spectra" and "microwave spectra" are sometimes used synonymously. The lines in rotational spectra are also expressed using several typical units, as the above examples showed. In the microwave region, it is typical (for historical, habitual, and practical reasons) to express transitions in units of frequency. In the microwave region, frequencies are in the megahertz (MHz) or gigahertz (GHz) range. It is not unusual to see rotational spectra displayed using frequency units. Figure 14.10 shows a pure rotational spectrum in terms of frequency.

Rotations frequently occur along with vibrations (which is why we use the phrase "pure rotational spectra" to differentiate those from rotational-vibrational spectra), so it is also customary to express the rotational transitions in a common unit of vibrational transitions, the wavenumber (in cm^{-1}). Figure 14.11 shows a rotational spectrum in terms of wavenumber. There is a potential problem when a rotational spectrum is displayed in terms of wavelength, because wavelength is not directly proportional to energy and the consistent spacing of rotational levels is not obvious. Figure 14.12 shows the same spectrum as Figure 14.11 but in terms of wavelength units. The equal spacing isn't obvious, despite the fact that each spectrum illustrates the same information. (This will be discussed further in our treatment of vibrational spectra, later in this chapter.)

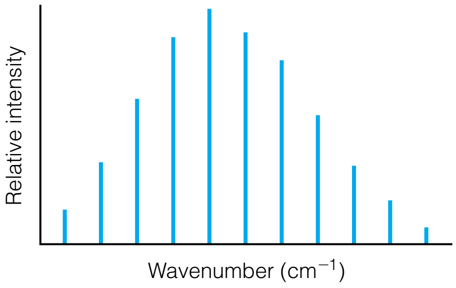


Figure 14.11 A simulated rotational spectrum, plotted in wavenumber units. Since wavenumbers are proportional to energy, the absorptions are evenly spaced.

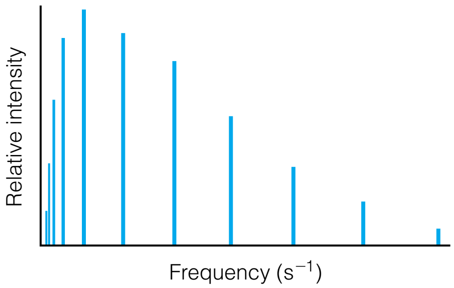


Figure 14.12 The same spectrum as Figure 14.11, but in frequency units. The spacing between lines is now not equal.

Rotational spectra, like those in Figures 14.11 and 14.12, show an interesting intensity pattern. The intensity pattern of rotational spectra is due to the number of molecules having a certain rotational state. This is called the *population* of the state. Because the population of each rotational state is different, the number of molecules absorbing radiation and becoming excited to the next state is different. This population difference is responsible for the varying intensities of each rotational spectral line.

The temperature determines the population of the rotational energy levels. Rotational levels are close enough in energy that thermal energy is sufficient to cause some of the molecules to be in excited rotational states. Therefore, there is an increased probability of a transition from those excited rotational states to the level next highest in J. At some value of J, however, the ability of the temperature to thermally populate rotational levels decreases. A statistical treatment of the energy levels indicates that the approximate maximum-populated J quantum number, $J_{\max}$, is

$$J_{\max} \approx \left(\frac{kT}{2B}\right)^{1/2} \tag{14.23}$$

where k is Boltzmann's constant (1.381×10^{-23} J/K), T is the absolute temperature of the sample, and B is the rotational constant (expressed in units of joules in this equation). This expression is in part due to the fact that the degeneracy of the rotational levels is $2J + 1$. If it were not, then the lowest rotational state would always be the most populated rotational state, and such intensity patterns as seen in Figures 14.11 and 14.12 would not appear. Equation 14.23 is an approximation. As a quantum number, J is limited to whole numbers, so some rounding off is usually necessary when using the above equation. Equation 14.23 allows one to estimate the temperature of a gas-phase sample from its rotational spectrum. (The effect of temperature on the population of energy levels will be a major topic of Chapter 17.)

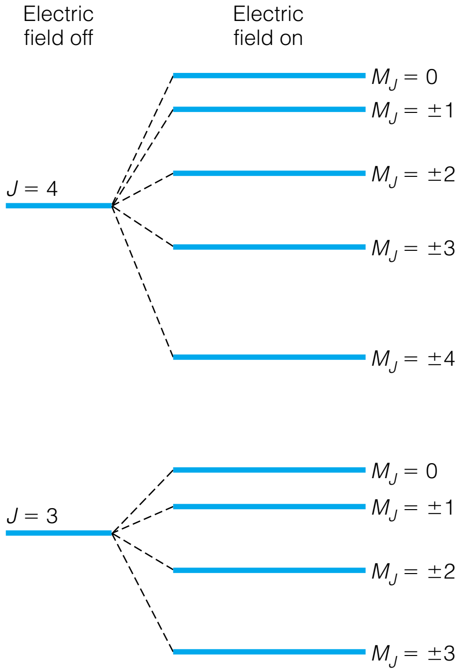


Figure 14.13 An applied electric field splits the degenerate same-J levels into different energy levels, depending on the M_J values. This is called the Stark effect. The changes in the energy levels are not necessarily to scale, since the change in energy is dictated by various parameters.

The energy of each rotational state has a degeneracy of $2J + 1$ due to the possible values of M_J. However, in the presence of a strong electric field in a particular direction, molecules rotating with different quantized values of angular momentum in that direction, indicated by the M_J values, will have slightly different energies. Absorptions or emissions due to rotational state transitions will appear to split into a larger number of lines, and the particular number of lines for each transition will be determined by the $\Delta M_J = 0, \pm1$ selection rule. This phenomenon is an example of the *Stark effect,* discovered by the German physicist Johannes Stark in 1913. In 1919, Stark was awarded a Nobel Prize for this discovery. This effect is another case of behavior that classical mechanics could not explain but quantum mechanics could. Examples of the splitting of the energy levels, the additional transitions, and a Stark effect spectrum are shown in Figures 14.13–14.15. It is important to note that the Stark effect depends on the z component of the angular momentum, identified with M_J, and is not dependent on the figure-axis component of angular momentum, identified with K.

Molecules that don't have a permanent dipole moment are rotating, of course, but they do not follow the gross selection rule for pure rotational spectra. Their rotations cannot be observed directly using microwave spectroscopy.

We now examine the rotational spectra of symmetric top molecules. The values for the rotational energy levels are given in equations 14.16 and 14.17 for symmetric tops. The specific selection rules for the change in J, K, and M_J quantum numbers were given above in equations 14.18–14.20. As with linear molecules, since M_J does not affect the rotational energy it will have no effect on the rotational spectrum unless the molecules are subjected to a strong electric field (that is, the Stark effect). Since the selection rule for K is that it must remain unchanged ($\Delta K = 0$), the difference in the rotational energies is dictated solely by changes in J:

$$\Delta E_{E(J)\rightarrow E(J+1)} = E(J+1) - E(J) = 2B(J+1) \qquad \textbf{(14.24)}$$

This equation is for absorption of electromagnetic radiation by either a prolate or an oblate top, where B is the rotational constant that appears twice in the three rotational constants for a symmetric top (remember, one of the rotational constants is unique and different from the other two). This is the same expression we determined for linear molecules. Again, the quantum number J refers to the lower-energy state involved in the transition.

This suggests that we can determine little more about the structure of symmetric tops other than a single rotational constant, even though symmetric tops have two distinct rotational constants. If molecules acted like perfect rigid rotors, this would be the case. But they're not perfect, and that does allow us to obtain additional information from a real spectrum. We will get to this in the next section.

By definition, molecules that are spherical tops do not have a permanent dipole moment, so they do not have a pure rotational spectrum. However, under some conditions they may have rotational absorptions superimposed in their vibrational spectrum.

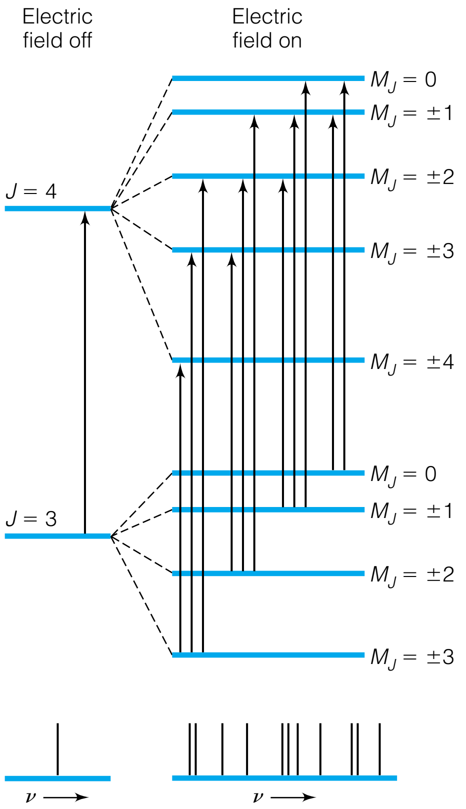


Figure 14.14 Imposition of an electric field can complicate an otherwise "simple" spectrum. For a diatomic molecule, the selection rule ΔM_J now dictates the possible transitions.

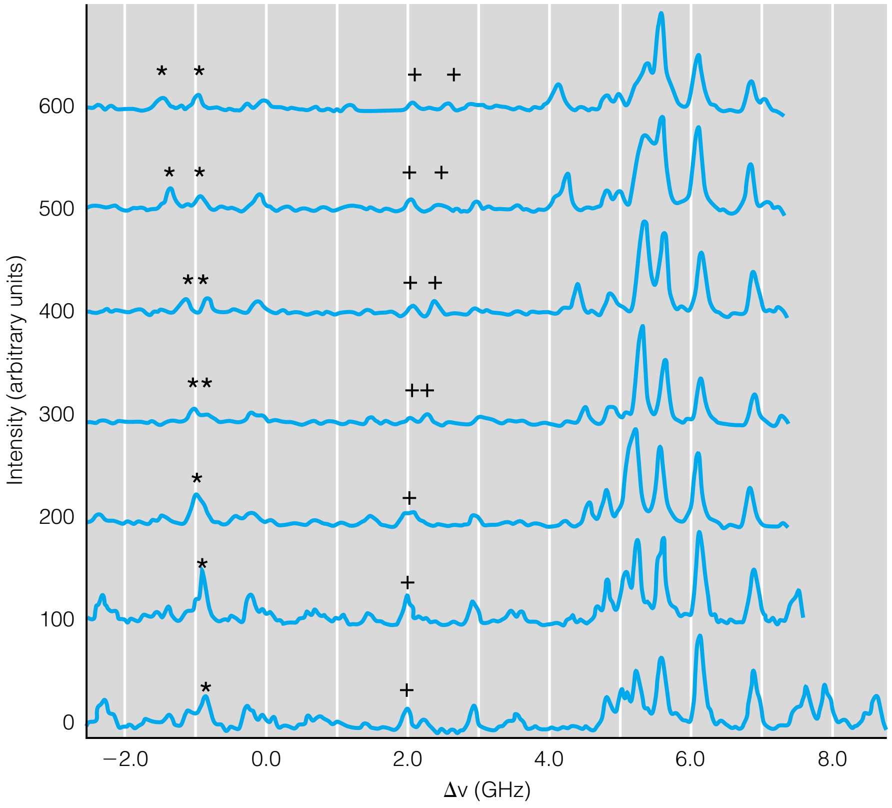


Figure 14.15 A real spectrum, showing the Stark effect on benzonitrile, C_6H_5CN. The + and * signs mark signals that are splitting due to the electric field. *Source:* Reprinted with permission from The American Chemical Society.

14.7 Centrifugal Distortions

Although the above sections suggest that rotational spectra are very simple, complications arise because molecules are real systems, not ideal ones. Although application of the ideal 3-D rigid rotor system to molecules works very well, it does not do a perfect job of describing rotational spectroscopy.

Perhaps the biggest single nonideal factor in rotational spectroscopy is the fact that molecules are not rigid rotors. It is assumed, for example, that the molecules have certain specific and unchanging bond distances. This is not the case. As molecules have larger and larger J quantum numbers (corresponding to higher and higher energies), they distort slightly but enough to change the energy levels noticeably away from the ideal values. This effect is called *centrifugal distortion.*

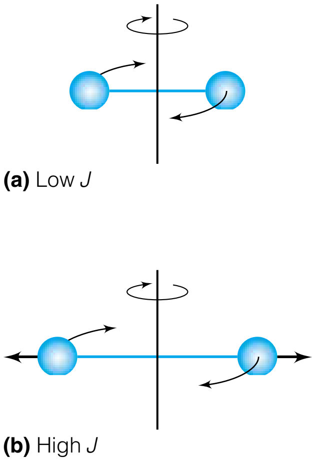


Figure 14.16 (a) Normal bond length in a diatomic molecule. (b) As the rotational quantum number increases, a centrifugal distortion causes the bond to stretch. This adds some nonideal component to the predicted rotational spectrum.

Consider the diatomic molecule in Figure 14.16a. As it rotates with a relatively low J quantum number, the chemical bond is strong enough to keep a fairly constant bond length. However, as Figure 14.16b shows, at large J the rotating molecule is distorted as the spinning atoms experience a sort of centrifugal force, like we would feel on a fast-spinning merry-go-round. This force contributes to a slight lengthening of the bond distance. Bond distances appear in the denominator of the rotational constants, used to define I, the moment of inertia. This lengthening of the bond therefore serves to lower the total energy of the rotational state, so instead of rotational spectral lines being exactly $2B$ apart, they begin to get less than $2B$ apart. The centrifugal distortion is thus observed as a shrinking of the distances between adjacent lines in a rotational spectrum.

The effect on the rotational energy of centrifugal distortion is proportional to $[J(J+1)]^2$ instead of $J(J+1)$. Indeed, if the centrifugal distortion depended on $J(J+1)$, it would be worked into the B rotational constant! What is usually done is to mathematically fit the rotational energies to a general equation having a form like

$$E_{\text{rot}} = BJ(J+1) - D_J J^2(J+1)^2 \tag{14.25}$$

where D_J is the *centrifugal distortion constant.* It usually is expressed in the same units as B, either MHz or GHz for frequency, or cm^{-1} for wavenumber. The positions of the rotational spectral lines are therefore given as

$$E_{J+1} - \mathrm{E}_J = \Delta E_{\text{rot}} = 2B(J+1) - 4D_J(J+1)^3 \tag{14.26}$$

where as usual the quantum number J refers to the quantum number of the lower-energy rotational state. Because the centrifugal distortion is less if the diatomic molecule bond is stiffer and therefore has a higher vibrational frequency (which will be introduced in the next section), the centrifugal distortion constant is often approximated by the following expression:

$$D_J \approx \frac{4B^3}{\tilde{\nu}^2} \tag{14.27}$$

where $\tilde{\nu}$ is the wavenumber of the vibration (in cm^{-1}) and B must also be expressed in units of cm^{-1}.

Equation 14.26 shows that the energy difference between rotational levels (energy differences are what spectra measure, after all) deviate from ideality by a factor based on the third power of the rotational quantum number J. Table 14.2 lists some experimental B values and D_J values for several diatomic molecules. D_J is typically very small, so effects due to centrifugal distortion are usually noticeable only if the spectra are for rotations of small molecules (like hydrogen), or if very high-energy rotational states are being probed.

Table 14.2 Rotational constants B and centrifugal distortion constants D_J for selected diatomic molecules[a]

Molecule	B	D_J
H_2	60.80	4.64×10^{-2}
D_2	30.42	1.159×10^{-2}
HCl	10.59	5.32×10^{-4}
HBr	8.473	3.72×10^{-4}
N_2	2.010	5.8×10^{-6}
NO	1.7046	$\sim 5 \times 10^{-6}$
O_2	1.446	4.95×10^{-6}

[a] All numbers have units of cm^{-1}.

Example 14.10

Find the energy of the $J = 10 \rightarrow J = 11$ transition for HCl for two cases: assume a pure rigid rotor behavior, and then include the centrifugal distortion constant. Use the value for B and D_J from Table 14.2. Compare the two results.

Solution

Using the rigid rotor approximation:

$$\Delta E = (21.18\ \text{cm}^{-1})(10 + 1) = 233.0\ \text{cm}^{-1}$$

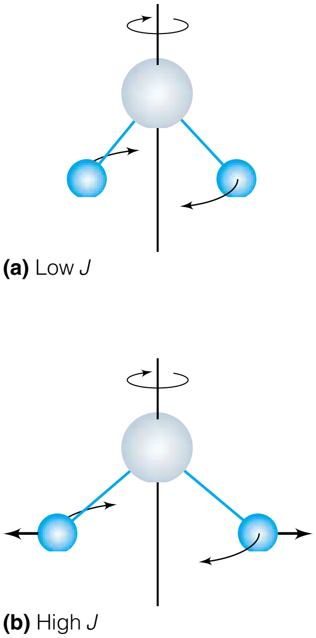
Using the expression for ΔE that explicitly includes the centrifugal distortion constant:

$$\Delta E = (21.18\ \text{cm}^{-1})(10 + 1) - 4(5.32 \times 10^{-4}\ \text{cm}^{-1})(10 + 1)^3$$

$$233.0 - 0.2575\ \text{cm}^{-1} = 232.7\ \text{cm}^{-1}$$

where the normal rules for significant figures in calculations have been applied. Notice that the change in the predicted ΔE isn't much, but it does get progressively larger as the rotational quantum number increases.

Diatomic and linear molecules aren't the only molecules that experience centrifugal distortions. Figure 14.17 shows diagramatically what happens to a water molecule when it rotates at high values of J: the atoms are forced to spread out somewhat due to centrifugal distortion, and this affects the values of rotational energy, as depicted in Figure 14.18. For prolate and oblate


(a) Low J

(b) High J

Figure 14.17 Centrifugal effect on a molecule of H_2O. Since water has three different rotations, it will have three different D_J values.

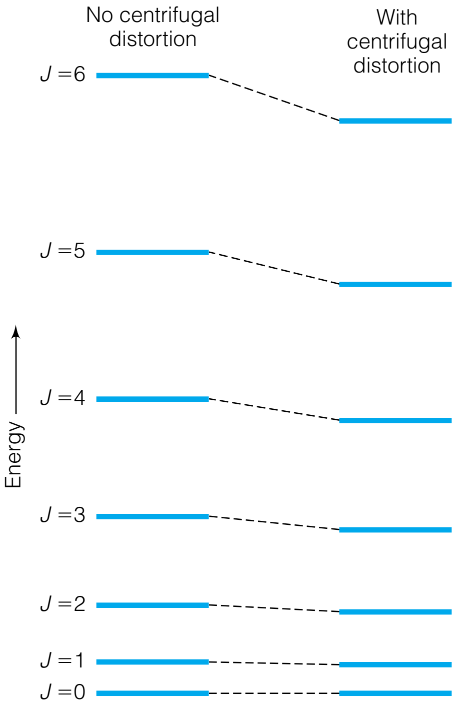


Figure 14.18 Effect of centrifugal distortion on the rotational energy levels. Because the distortion depends on $J^2(J + 1)^2$, higher J values show a larger deviation from ideal rotational energies. This figure gives the general behavior of the rotational energy levels and is not to scale for H_2O.

symmetric tops, however, the situation is somewhat more complicated because there are two different moments of inertia and therefore two series of rotational spectra. As the molecule is distorted about one rotational axis, it affects the moment of inertia in another axis. Centrifugal distortions of nonlinear molecules are therefore extremely complicated and will not be considered here.

14.8 Vibrations in Molecules

For a molecule having N atoms, it is necessary to use an x, a y, and a z coordinate to describe the positions of each of the atoms, and so such a molecule requires a total of $3N$ coordinates to describe its position in space. Such a situation is shown in Figure 14.19.

For changes in position, the number of necessary changes in coordinates is the same. For a molecule having N atoms, each atom's change in position can be broken down into a change in x, a change in y, or a change in z coordinate. (These changes are simply written as Δx, Δy, and Δz for each of the N atoms.) These changes in coordinates may have different values, so an N-atom molecule needs a total of $3N$ changes in coordinates to describe its motion. Such a situation is shown in Figure 14.20. Note how this corresponds to Figure 14.19. Because the atoms are free to move in $3N$ different independent ways, we say that the molecule has $3N$ degrees of freedom.

It turns out that we can always choose the coordinates so that the combined motion of all atoms for three of the $3N$ ways corresponds to all of the atoms moving in either the x, the y, or the z direction. That is, they describe *translations* of the molecule as a whole. Figure 14.21 shows these three translational degrees of freedom. Since the entire molecule moves in space, we can describe these motions as translations of the center of mass of the molecule. In translational motions, the atoms of the molecule are not moving with respect to each other.

These same changes in coordinates can simultaneously be chosen so that two (for a linear molecule) or three (for a nonlinear molecule) of the combined motions of all atoms correspond to rotations of the molecule about a

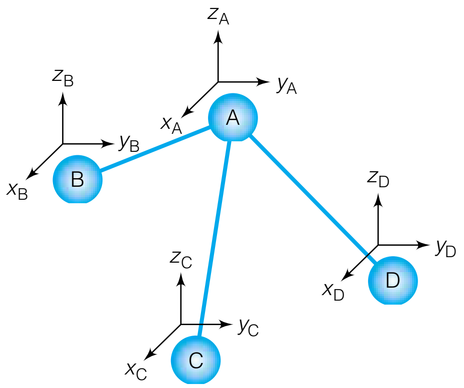


Figure 14.19 For a molecule having N atoms, a total of $3N$ coordinates is necessary to describe the position of atoms in the molecule. The four atoms shown here require $3 \times 4 = 12$ total coordinates. Therefore, we say that this molecule has 12 degrees of freedom.

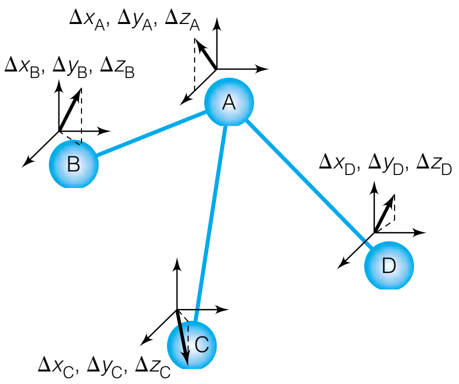


Figure 14.20 For any general motion of a molecule, $3N$ changes in coordinates are necessary to describe the motion. Each atom requires a Δx, a Δy, and a Δz to describe its motion.

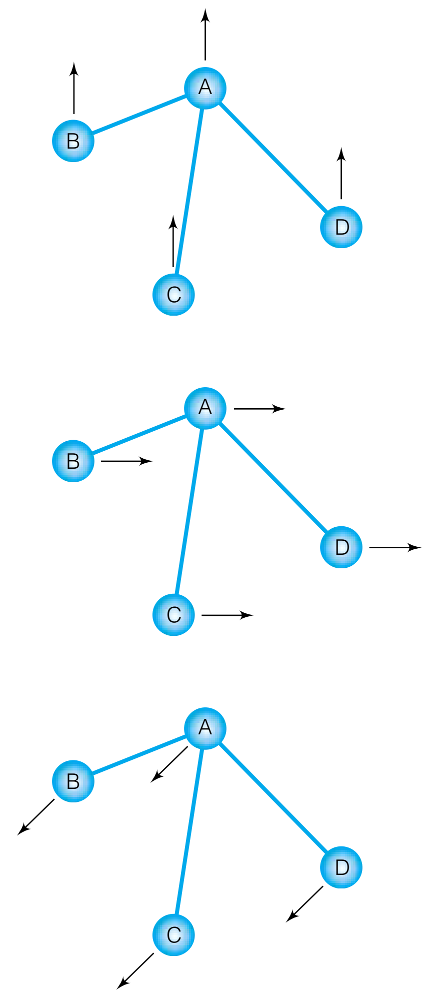


Figure 14.21 Three of the $3N$ degrees of freedom correspond to translations of the molecule as a whole.

molecular axis. Figure 14.22 shows these *rotational degrees of freedom* for linear and nonlinear molecules. For rotations, as for translations, the atoms of the molecule are moving together in such a way as to move the molecule. Unlike translations, in rotations the center of mass of the molecule is not moving in space. However, like the translational degrees of freedom, again the atoms are not moving with respect to each other.

This leaves either $3N - 5$ (for linear molecules) or $3N - 6$ (for nonlinear molecules) combinations of the motions of the atoms of the molecule. In these combinations, the atoms are moving with respect to each other, but the center of mass of the entire molecule does not change. These internal atomic motions are the *vibrational degrees of freedom,* or more simply the *vibrations,* of the molecule.

There are many ways to describe the possible motions of the atoms in a molecule. However, a mathematical treatment of vibrations shows that there will always be a way to assign the changes in coordinates such that all of the possible motions of the atoms can be broken down into $3N - 5$ (for linear molecules) or $3N - 6$ (for nonlinear molecules) independent motions where for each motion the frequency of every atom's vibration is exactly the same. Such coordinate changes are called *normal modes of vibration,* or just the *normal modes.*

In vibrational spectroscopy, the frequencies of the vibrating atoms in the molecule are probed. The changes in the energies of the vibrations are such that the radiation typically used is in the infrared region of the spectrum. Hence, IR spectroscopy is usually synonymous with vibrational spectroscopy. Very low frequency vibrations will be detected in the microwave region of the spectrum, whereas high-frequency changes impinge on the visible spectrum. As with rotational spectroscopy, the wavenumber (cm^{-1}) unit is common, but so is the unit that describes the wavelength of the light involved, usually expressed as micrometers or microns.

Why do linear molecules have a different term ($3N - 5$ instead of $3N - 6$)? Recall that linear molecules have no defined rotation about their internuclear axis, so they lack a rotational degree of freedom. This lack is made up for by having an extra vibrational degree of freedom. We will find that linear molecules have at least one vibration that moves perpendicular to another vibration of the same frequency (and therefore they have the same energy: they are degenerate).

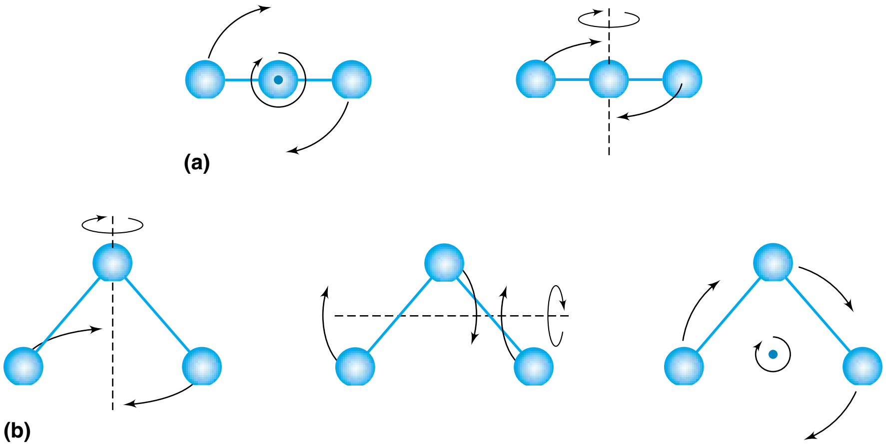


Figure 14.22 The rotations in the $3N$ degrees of freedom are either (a) two for linear, or (b) three for nonlinear.

Example 14.11

Determine the number of vibrational degrees of freedom for the following molecules.

a. Hydrogen chloride, HCl
b. Hydrogen sulfide, H_2S
c. Benzene, C_6H_6
d. Acetylene, C_2H_2
e. The sulfate ion, $SO_4{}^{2-}$
f. Hydrogen peroxide, H_2O_2

Solution

a. By definition, HCl is linear, therefore it has $3(2) - 5 = 1$ vibrational degree of freedom.
b. H_2S is not linear, so it has $3(3) - 6 = 3$ vibrational degrees of freedom.
c. Benzene has $3(12) - 6 = 30$ degrees of freedom. Its high symmetry will simplify matters, though.
d. C_2H_2 is linear, so it has $3(4) - 5 = 7$ vibrational degrees of freedom.
e. The sulfate ion is not linear: 9 vibrational degrees of freedom.
f. Hydrogen peroxide is nonlinear: 6 vibrational degrees of freedom.

The solutions above hint that symmetry has a great deal to do with the number of truly unique vibrational degrees of freedom. Consider benzene, which is planar and has D_{6h} symmetry. Because of its symmetry, certain vibrations of benzene are identical to each other and have the same vibrational frequency. This means that there will be fewer than 30 unique vibrational frequencies in this molecule. (There are in fact only 20 unique frequencies.) Symmetry will have similar ramifications for vibrations in other molecules, too.

14.9 The Normal Modes of Vibration

The vibrations of all molecules can be described in terms of independent motions such that for each motion the frequency of vibration for all atoms is the same. These are the normal modes of vibration. Why are the normal modes so important? There are several reasons, but perhaps the most important one is this: to a good approximation, the frequencies of light that are absorbed due to vibrational motions of atoms in molecules are those that have the same frequencies as the normal modes of vibration.

Consider the vibration of the two atoms in the HCl molecule (Figure 14.23). There is only a single vibrational mode, where the hydrogen and chlorine atoms are alternately closer and farther away from each other (a "stretching mode"). For simplicity, the arrows indicating an atom's direction of motion point in a single direction only. It is understood that in the course of a full vibration the atoms move in the opposite direction also. Note too that the lengths of the arrows are different: the hydrogen atom is shown "moving" farther than the chlorine atom. This preserves the position of the center of mass of the molecule, so it does not change.

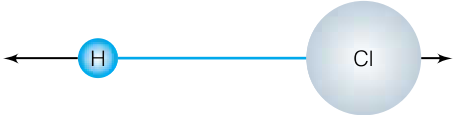


Figure 14.23 The single vibration of HCl has the hydrogen and chlorine atoms moving alternately back and forth. The hydrogen's movement is much larger than the chlorine's, because of H's much higher mass.

A single vibration agrees with the $3N - 5$ expression for the number of vibrations in a molecule: for HCl, $3N - 5$ is $3(2) - 5$, which equals 1. The two atoms in HCl can be thought of as a classical harmonic oscillator composed of two masses (the two atoms) connected by a spring (the chemical bond). This harmonic oscillator vibrates with a frequency of about 8.65×10^{13} Hz, or

86,500 GHz. Therefore, it absorbs only the light that has the same frequency: 86,500 GHz. Light of this frequency has a wavelength of about 3.46 micrometers, or 3.46 microns, which is in the infrared region of the spectrum. In units of wavenumbers, this light has a frequency of 2886 cm^{-1}.

Consider the possible vibrations of the three atoms in the H_2O molecule, however. This molecule has $3(3) - 6 = 3$ vibrational degrees of freedom. What are they? One can imagine that the three atoms in water move about in a complicated dance that might be difficult to understand. However, the vibrational spectrum of water shows three and only three distinct absorptions: at 3756, 3657, and 1595 cm^{-1}. These must correspond to the frequencies of the atoms in the three normal modes of water. The motions of the atoms in these normal modes (which can be determined mathematically) are illustrated in Figure 14.24. Notice that the vectors illustrated have different lengths so as to keep the center of mass in the same position. Again, only part of the motion is illustrated. The atoms also move in the reverse direction in the course of a single vibration. The normal vibrational modes of H_2O are generally referred to as (in decreasing order of wavenumber) the asymmetric stretching mode, the symmetric stretching mode, and the bending mode.

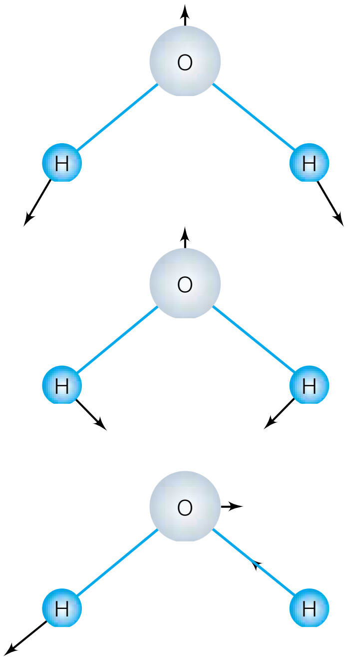


Figure 14.24 The three normal modes of H_2O. The lengths of the vectors indicate the relative distances that each atom moves. The actual distance that each atom moves is very small, less than 0.1 Å.

No matter how complicated the molecule, the motions of the atoms with respect to each other can be treated solely as if those atoms were moving as shown by the normal modes. This allows us to consider *only* the normal modes. More importantly, because of symmetry, some of the normal modes of large molecules are exactly the same as others. Consider again the C–H stretches of benzene, C_6H_6. Because of the sixfold symmetry of benzene, we might expect that they can be described equivalently, and to a certain extent this is true. As such, these normal modes have the same vibrational frequency. The total number of *unique* normal modes therefore depends on two things: the number of atoms in the molecule (as indicated by the $3N - 5$ or $3N - 6$ number of normal modes) and the symmetry of the molecule. The higher the symmetry, the fewer the number of independent normal modes.

14.10 Quantum-Mechanical Treatment of Vibrations

When one considers a diatomic molecule, it can be compared to the ideal harmonic oscillator as defined by Hooke's law:

$$F = -kx \tag{14.28}$$

where the force F acting against a displacement x is proportional to x. (We are ignoring the vector aspects of F and x here.) The proportionality constant, k, is called the *force constant*. It has units of force/distance, like N/m or mdyn/Å. An ideal harmonic oscillator is also defined as having a potential energy of

$$V = -\int F\,dx = \tfrac{1}{2}kx^2 \tag{14.29}$$

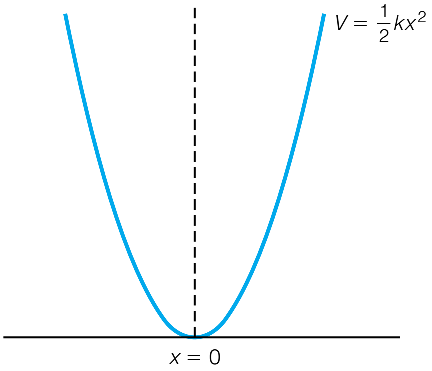


Figure 14.25 Potential energy diagram for an ideal harmonic oscillator. Usually, this diagram is applicable only for low-energy (that is, low quantum number) vibrations.

A plot of a potential energy versus displacement is shown in Figure 14.25. In the first approximation, diatomic molecules can be considered in terms of a quantum-mechanical harmonic oscillator having reduced mass μ, which, recall, is related to the two masses of the atoms m_1 and m_2:

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2} \tag{14.30}$$

or, equivalently,

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

By making this ideal harmonic oscillator assumption, we make the wavefunctions and energies for the ideal harmonic oscillator directly applicable to the diatomic molecule's vibrations! In particular, since spectroscopy deals with differences in the energy states, we are particularly interested in the fact that

$$E_{\text{vib}} = h\nu(v + \tfrac{1}{2}) \qquad v = 0, 1, 2, 3, \ldots \tag{14.31}$$

where h is Planck's constant, ν is the classical frequency as predicted by Hooke's law, and v is the vibrational quantum number.† (Be careful not to confuse ν with v.) That is, we expect that the vibrational energy of the diatomic molecule is *quantized* and given by equation 14.31 above. If the energies of the vibrational states are quantized, then the *differences* in the energies will have only certain values.

Diatomic molecules are particularly easy to treat quantum-mechanically because they are easily described in terms of the classical harmonic oscillator. For example, the expression

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{14.32}$$

which relates the classical force constant and reduced mass of the oscillator to its frequency, is a valid mathematical tool. It is relatively easy to extend some concepts to other vibrational motions of larger molecules: the vibrations act as ideal harmonic oscillators that have certain wavefunctions and certain quantized energies. However, normal modes are vibrations of all atoms in a molecule, not just two, so expressions like equation 14.32 aren't directly applicable even if the idea of a force constant for a polyatomic motion is used. On the other hand, many normal modes are largely motions of only a few connected atoms of a large molecule, so it is not uncommon to hear of "C–H stretches" or "CH_2 bends" or such localized types of motions even for large molecules. Technically, such labels are incorrect, but practically they are useful in *qualitatively* describing the normal mode of the molecule.

Example 14.12

Assuming that the vibrational frequency of 2886 cm^{-1} ($8.652 \times 10^{13}\ s^{-1}$) for hydrogen chloride is $^{1}H^{35}Cl$, predict the vibrational frequencies for $^{1}H^{37}Cl$ and $^{2}H^{35}Cl$. Assume that the molecule is an ideal harmonic oscillator and that the force constant does not change upon isotopic substitution. (Such assumptions are common in vibrational spectroscopy.)

Solution

If the molecule is acting like an ideal harmonic oscillator and the force constant is not changing, then for the classical frequency of the $^{1}H^{35}Cl$ oscillator we have

$$8.652 \times 10^{13}\ s^{-1} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

and

$$\nu^* = \frac{1}{2\pi}\sqrt{\frac{k}{\mu^*}}$$

---

†In Chapter 11, we used n for the quantum number for the harmonic oscillator.

where the asterisk is used to indicate an isotopic substitution. When we take a ratio of the above two equations, such treatments will cancel each other and we can get

$$\frac{\nu^*}{8.652 \times 10^{13}\ \text{s}^{-1}} = \frac{\dfrac{1}{2\pi}\sqrt{\dfrac{k}{\mu^*}}}{\dfrac{1}{2\pi}\sqrt{\dfrac{k}{\mu}}}$$

which reduces to

$$\frac{\nu^*}{8.652 \times 10^{13}\ \text{s}^{-1}} = \sqrt{\frac{\mu}{\mu^*}}$$

Because the frequency ratio is related to a reduced mass *ratio*, it doesn't matter what units we use to express the reduced mass ratio. Rather than express the reduced masses in atomic values (on the order of 10^{-27} kg or so), we can simply use grams per mole as the unit of mass. The reduced mass of $^1H^{35}Cl$ is therefore 0.9722 (grams per mole), whereas the reduced mass of $^1H^{37}Cl$ is 0.9737 (grams per mole). The above equation becomes

$$\frac{\nu^*}{8.652 \times 10^{13}\ \text{s}^{-1}} = \sqrt{\frac{0.9722\ \text{g/mol}}{0.9737\ \text{g/mol}}}$$

The units cancel, yielding a ratio that has the same value no matter what units of mass are used. Evaluating:

$$\frac{\nu^*}{8.652 \times 10^{13}\ \text{s}^{-1}} = 0.9992$$

This rearranges to $\nu^* = 8.659 \times 10^{13}\ \text{s}^{-1}$, or 2884 cm^{-1} (to four significant figures). This is a relatively insignificant change, although it is easily detectable. However, for $^2H^{35}Cl$:

$$\frac{\nu^*}{8.652 \times 10^{13}\ \text{s}^{-1}} = \sqrt{\frac{0.9722\ \text{g/mol}}{1.891\ \text{g/mol}}}$$

$$\frac{\nu^*}{8.652 \times 10^{13}\ \text{s}^{-1}} = 0.7170\ \text{(unitless)}$$

$$\nu^* = 6.203 \times 10^{13}\ \text{s}^{-1} \quad \text{or} \quad 2069\ \text{cm}^{-1}\ \text{(to four significant figures)}$$

This predicts a shift of over 800 wavenumbers. The measured vibrational frequency of $^2H^{35}Cl$ is 2091 cm^{-1}, which agrees with the assumption of an ideal system.

It is not necessary to convert a wavenumber value into a frequency value when doing an example like the one above, because the two quantities are directly proportional to each other. Also, even if a molecule isn't a diatomic molecule, and even though a normal mode consists of the vibrations of all atoms in the molecule, in many cases for stretching-type motions a "diatomic approximation" can be made for isotopic substitution. The next example illustrates.

Example 14.13

If the symmetric O–H stretch for water occurs at 3657 cm^{-1}, predict the frequency of the O–D stretch of D_2O (D is ^2H) assuming that the O–H stretch acts as a diatomic species.

Solution

We can use a ratio similar to the one used in Example 14.12, in terms of the reduced masses of the molecules, and use the wavenumber value directly:

$$\frac{\tilde{\nu}^*}{3657\ \mathrm{cm}^{-1}} = \sqrt{\frac{\mu}{\mu^*}}$$

Considering the O–H and O–D bonds, the reduced masses (in units of grams per mole) substituted into the above expression yield

$$\frac{\tilde{\nu}^*}{3657\ \mathrm{cm}^{-1}} = \sqrt{\frac{0.9412\ \mathrm{g/mol}}{1.778\ \mathrm{g/mol}}}$$

$$\frac{\tilde{\nu}^*}{3657\ \mathrm{cm}^{-1}} = 0.7276$$

$$\tilde{\nu}^* = 2661\ \mathrm{cm}^{-1}$$

Experimentally in the vibrational spectrum of D_2O, the symmetric O–D stretch has a vibrational frequency of 2671 cm^{-1}, which shows that the diatomic approximation applied to parts of molecules can be very good. Such approximate calculations are useful in understanding vibrational spectra of molecules.

14.11 Selection Rules for Vibrational Spectroscopy

As with rotational spectroscopy, there are several ways of stating selection rules for spectral transitions involving vibrational states of molecules. There is a gross selection rule, which generalizes the appearance of absorptions or emissions involving vibrational energy levels. There is also a more specific, quantum-number-based selection rule for allowed transitions. Finally, there is a selection rule that can be based on group-theoretical concerns, which were not considered for rotations.

Recall that light is an oscillating electromagnetic field. It can interact with other oscillating electromagnetic fields, like the dipole moment of a molecule. This interaction dictated our gross selection rule for pure rotations: the molecule must have a permanent dipole moment in order to have a pure rotational spectrum. This is because the rotating dipole acts as an oscillating electric field, not changing in its magnitude but in its direction. As a vector, the dipole moment can oscillate by changing either its magnitude, or its direction, or both in order to be detectable by another oscillating electromagnetic field, the light.

For vibrations, the key to interacting with light is based on the *changing magnitude* of the dipole moment of the molecule during the vibration. The *dipole moment* of a molecule is defined as the charge differential times the distance between the differential charges. The distance between charges changes as the atoms of the molecule vibrate. As it changes, an oscillating electric field is created, which can interact with the electromagnetic field of light.

Suppose there is no dipole moment changing its magnitude due to changing distance. There may be a fleeting, nonpermanent dipole present as a result of the symmetry-destroying distortions imposed on a molecule during a vibrational motion. This will still be enough to interact with light. If, however, there is not either a change in dipole magnitude or directions, then there is no oscillating field to interact with the light, and no light is absorbed or emitted.

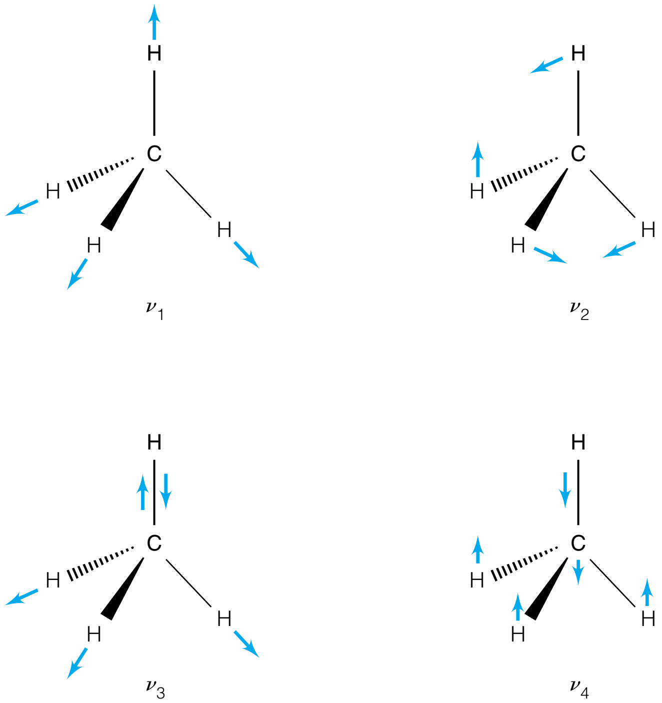


Figure 14.26 Normal modes of vibration for methane, CH_4. Although methane does not have a permanent dipole moment, some of the vibrations distort the molecule so that a fleeting dipole moment is present. These vibrations absorb infrared light and appear in a vibrational spectrum of methane.

Therefore, the gross selection rule for vibrations is the presence of a dipole moment that changes during the course of the vibration: a *varying dipole moment* is required.

Note that this does not imply that the molecule must have a permanent dipole moment in order to have a vibrational spectrum. Consider the methane molecule, CH_4. It has no permanent dipole moment, thanks to its tetrahedral symmetry. However, in the course of the vibrations of the atoms in the molecule (see Figure 14.26), fleeting dipole moments are present as the atoms distort the molecule. In this way, not only the magnitude but also the direction of such fleeting dipole moments is changing. Methane absorbs richly in the infrared region of the spectrum due to its vibrations. CO_2 is a linear molecule. It has no permanent dipole moment, but during the course of some of its molecular vibrations it has a fleeting nonzero dipole moment that allows for light to be absorbed. However, for one specific normal mode of CO_2, there is no net dipole moment change because both oxygen atoms are moving back and forth with respect to the carbon atom in phase, by the same amount (this is the so-called symmetric stretching motion of CO_2). This particular vibrational motion of the molecule is not active in absorbing infrared light. (The vibrational motions of CO_2 are particularly important in carbon dioxide's behavior as a greenhouse gas. Even though CO_2 has no permanent dipole moment, it absorbs energy in the form of infrared light due to its vibrational motions.)

Homonuclear diatomic molecules do not absorb or emit radiation due to vibrational state transitions. By definition, homonuclear diatomic molecules have no dipole moment and no changing dipole moment as the two atoms vibrate. Other methods are necessary to observe vibrational energy levels directly.

Example 14.14

Which of the following molecules will have pure vibrational spectra?

a. Hydrogen sulfide, H_2S

b. Oxygen, O_2

c. Ozone, O_3

d. Hydrogen chloride, HCl

e. acetylene, C_2H_2

Solution

a. Hydrogen sulfide is a bent molecule, like water. It has a permanent dipole moment varies as the molecule vibrates. It will show a pure vibrational spectrum.

b. Elemental oxygen, a homonuclear diatomic, will not have a pure vibrational spectrum.

c. Ozone is a bent molecule, which will have a permanent dipole moment. Like H_2S, ozone's dipole moment will change during the course of a vibration, so we would expect that ozone will have a detectable vibrational spectrum.

d. Hydrogen chloride is diatomic, but it has a dipole moment whose magnitude will change as the two atoms change distance. Therefore, it is expected to have a vibrational spectrum.

e. Acetylene is linear, but like carbon dioxide it is expected that some of its vibrations will produce a fleeting dipole moment. We therefore expect that acetylene will have a pure vibrational spectrum.

There is a more specific selection rule that depends on the quantum number for the vibrational state, v. Since the normal modes of vibration are independent of each other (they are orthogonal to each other), this selection rule is applicable to one normal mode at a time. That is, we will consider the application of this new selection rule to each individual normal mode of vibration. The selection rule does not address simultaneous changes in more than one normal mode of vibration. As indicated in section 14.2, such specific selection rules are group-theoretical. The transition moment integral for vibrations is

$$\int \Psi_{v'}\hat{\mu}\Psi_v \, d\tau$$

where v and v' represent the vibrational quantum numbers of the two vibrational states involved, and $\hat{\mu}$ is the electric dipole operator. In order for this integral to be nonzero for an allowed transition, the following change in quantum number v is allowed:

$$\Delta v = \pm 1 \tag{14.33}$$

This selection rule is applicable to each normal mode of vibration. In absorption spectroscopy, the change is +1. This assumes that the normal mode acts as an ideal harmonic oscillator. Real molecules do not act as ideal harmonic oscillators, so in some cases it is not uncommon to detect $\Delta v = \pm 2, \pm 3, \ldots$, transitions. Such observations are part of what is called *overtone spectroscopy.* Partly because of the selection rule in equation 14.33, detection of overtones is difficult because many such absorptions are only weakly represented in a vibrational spectrum. Lasers, with their high intensities, are frequently utilized in overtone spectroscopy. However, the majority of vibrational spectroscopy deals with transitions following equation 14.33.

Because of the energy involved in vibrational transitions, almost all vibrational spectra measured at room temperature are probing transitions of vibrations from a $v = 0$ lowest-energy *ground state* to the $v = 1$ first *excited state.* Such transitions are called the *fundamental vibrational transitions.* In some cases, higher vibrational states are significantly populated due to thermal energy, either because the vibrational energy state itself is small or the temperature is large. Under such conditions, transitions like $v = 1 \rightarrow v = 2$ or higher vibrational levels can be probed. Such absorptions are called *hot bands.*

If the normal mode is acting as an ideal harmonic oscillator, then we can use the quantum-mechanical expressions that describe its energy. Recall that for an ideal harmonic oscillator,

$$E(v) = h\nu(v + \tfrac{1}{2})$$

where v is the vibrational quantum number, ν is the classical frequency of the oscillator, and h is Planck's constant. Therefore, it is easy to show that the change in energy between adjacent energy levels is

$$E(v + 1) - E(v) \equiv \Delta E = h\nu \qquad \textbf{(14.34)}$$

A vibrational spectrum is composed of absorptions that correspond to $h\nu$, where ν is the classical frequency of the vibration. Note the very broad applicability of equation 14.34: it is independent of the quantum number v. For an ideal harmonic oscillator, the allowed transitions occurring for any one normal mode all have the same ΔE, and so all will absorb the same frequency of light.

If a molecule shows transitions for $\Delta v = \pm 2, \pm 3, \ldots, \pm n$, then it is easy to show that for an n-fold change in the quantum number v,

$$\Delta E = nh\nu \qquad \textbf{(14.35)}$$

Changes in vibrational energy should be exact multiples of the $\Delta v = 1$ transition. However, real normal vibrations are not ideal (which is why such transitions are observed occasionally in the first place), so absorptions due to overtone transitions are usually less than an integral number of $h\nu$. This deviation is a measure of anharmonicity, which we will consider in the next section. Table 14.3 lists the absorptions due to the fundamental and overtone vibrational transitions for HCl (g). Also listed are the various multiples of the fundamental vibrational frequency, and the variance from the multiple as shown by experiment. Note how the overtone absorptions get farther and farther from ideal. The fact that $\Delta v > 1$ is possible (although to a much lesser extent than $\Delta v = 1$) and the variance from exact multiples of the fundamental vibrational frequency are both reminders that molecules are not true harmonic oscillators. They are anharmonic oscillators. The use of the ideal harmonic oscillator system in describing molecular vibrations is an approximation—but a good approximation.

Table 14.3 Fundamental and overtone vibrational absorptions of HCl (g)

Transition	Frequency (cm^{-1})	Fundamental multiple	Variance
$v = 0 \rightarrow v = 1$	2,885.98	—	—
$v = 0 \rightarrow v = 2$	5,667.98	2(2,885.98) = 5,771.96	103.98
$v = 0 \rightarrow v = 3$	8,346.78	3(2,885.98) = 8,657.94	311.16
$v = 0 \rightarrow v = 4$	10,922.81	4(2,885.98) = 11,543.92	621.11
$v = 0 \rightarrow v = 5$	13,396.19	5(2,285.98) = 14,429.90	1,033.71

Source: R. J. Sime, *Physical Chemistry: Methods, Techniques, and Experiments,* Saunders, Philadelphia, 1990. Referenced there as D. H. Rank, D. P. Eastman, B. S. Rao, and T. A. Wiggins, *J. Opt. Soc. Am.,* 1962, 52: 1–7.

14.12 Vibrational Spectroscopy of Diatomic and Linear Molecules

For infrared absorption spectroscopy of diatomic molecules, only *heteronuclear* diatomic molecules show a vibrational spectrum. Their spectra are relatively simple, since there is only one vibration: the motion of the two atoms back and forth about their center of mass. This is a good example of a stretching vibrational mode. Table 14.4 lists, among other data, the stretching vibrations for a series of gaseous diatomic molecules.

To a first approximation, the vibrations of diatomic molecules can be treated as harmonic, Hooke's-law-type oscillators. That is, as the molecules are moving back and forth about their center of mass, the force opposing the motion is proportional to the distance away from some minimum-energy, equilibrium distance. Figure 14.27 shows a plot of the potential energy curve, equal to $\frac{1}{2}kx^2$, for ideal oscillators. Superimposed on this potential energy curve are the values of the vibrational energy for the oscillator. For an ideal harmonic oscillator, the vibrational levels are spaced equally, which is consistent with equation 14.34. The vibrational force constant, k, is a measure of the curvature of the potential energy plot. It can easily be shown that

$$\frac{\partial^2 V}{\partial x^2} = k$$

Therefore, the larger the force constant, the narrower the potential energy curve.

However, real molecules are not ideal systems. A more accurate potential energy curve for the vibration of diatomic molecules resembles the curve for a real molecule in Figure 14.28. The harmonic potential energy curve is superimposed for comparison. At low vibrational energies the curve is close to ideal, but at higher vibrational energies the potential energy curve is much wider than for the ideal harmonic oscillator. As a result, the vibrational energy levels, shown in the figure, begin to get closer and closer together. This is the trend observed in Table 14.3 for the energies of the HCl vibration. In reality, our oscillator is not harmonic but *anharmonic.* Also, at some point the molecule has enough energy that the two atoms move apart—and never move back toward each other. The molecule has dissociated, and the amount of energy required to do this is called the *dissociation energy.* No quantized vibrational levels exist above the dissociation energy limit. An ideal harmonic oscillator does not have a dissociation energy until one gets to $v = \infty$.

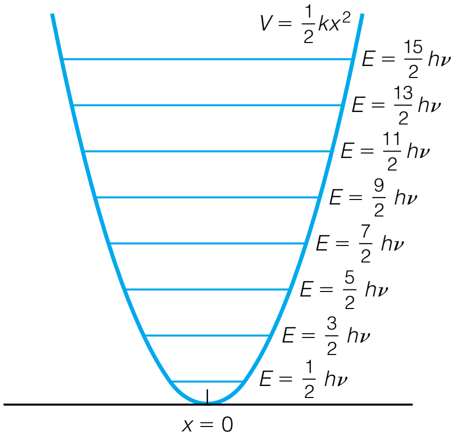


Figure 14.27 For an ideal harmonic oscillator, the potential energy equals $\frac{1}{2}kx^2$ and the quantized energy levels are equally spaced.

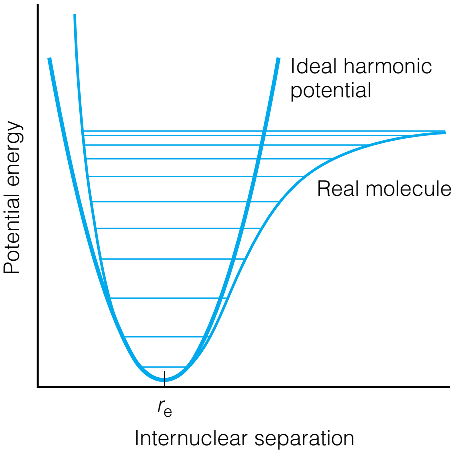


Figure 14.28 A more realistic potential energy surface for the vibration of a molecule is superimposed on the ideal harmonic oscillator curve. Only at low vibrational quantum numbers does the ideal potential energy curve adequately approximate the real system. Note how the vibrational energy levels get closer and closer together as the vibrational quantum number increases.

Table 14.4 Vibrational parameters of various heteronuclear diatomic molecules[a]

Molecule	$\tilde{\nu}_e$ (cm^{-1})	$x_e\nu_e$ (cm^{-1})	Internuclear distance, Å
HF	4138.52	90.07	0.9171
HCl	2989.74	52.05	1.275
HBr	2649.67	45.21	1.413
OH	3735.21	82.81	0.9706
OD	2720.9	44.2	0.9699
NO	1904.03	13.97	1.1508
CO	2170.21	13.46	1.1281
LiH	1055.12	13.22	1.5949

Source: G. Herzberg. *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules.* Van Nostrand Reinhold, New York, 1950.

[a] See also Table 14.2

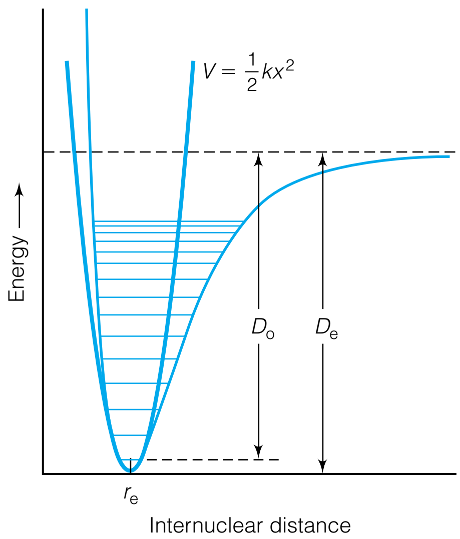


Figure 14.29 The Morse potential is a better fit to the potential energy curve of a real molecule than is the harmonic oscillator potential energy surface, superimposed.

Instead of using $V = \frac{1}{2}kx^2$ as the vibrational potential energy function of real diatomic molecules, it is common to use the following expression:

$$V = D_e(1 - e^{-a(r-r_e)})^2 \tag{14.36}$$

This potential is called the *Morse potential* and is plotted in Figure 14.29, along with the potential curve for the ideal harmonic oscillator. D_e is the molecular dissociation energy as measured to the *bottom* of the potential energy curve, as shown in Figure 14.29. The constant a is related to the force constant k of the molecule by the expression

$$a = \left(\frac{k}{2D_e}\right)^{1/2} \tag{14.37}$$

The constant a has units of (length)$^{-1}$.

Example 14.15

Predict the value of the Morse potential constant a for HCl if its D_e is 445.0 kJ/mol and the force constant is 5.16 mdyn/Å.

Solution

Although a straightforward substitution into equation 14.37 is warranted, the units for the given values are inconsistent. Consider D_e first. We need to find the amount of energy to dissociate a single HCl molecule, not a mole of molecules. The following steps provide the conversion:

$$445.0\ \text{kJ/mol}\ \frac{1000\ \text{J}}{1\ \text{kJ}}\ \frac{1\ \text{mol}}{6.02 \times 10^{23}\ \text{molecules}} = 7.39 \times 10^{-19}\ \text{J}$$

for one molecule. The force constant, 5.16 mdyn/Å, also needs to be converted (10^5 dynes = 1 newton):

$$5.16\ \text{mdyn/Å}\ \frac{1\ \text{dyn}}{1000\ \text{mdyn}}\ \frac{1\ \text{N}}{10^5\ \text{dyn}}\ \frac{10^{10}\text{Å}}{1\ \text{m}} = 516\ \text{N/m}$$

Substituting these numbers into equation 14.37, and recalling that a joule equals a newton · meter:

$$a = \left(\frac{516\ \text{N/m}}{2 \cdot 7.39 \times 10^{-19}\ \text{J}}\right)^{1/2} = \left(\frac{516\ \text{N/m}}{2 \cdot 7.39 \times 10^{-19}\ \text{N·m}}\right)^{1/2}$$

$$= \left(\frac{3.49 \times 10^{20}}{\text{m}^2}\right)^{1/2}$$

$$a = 1.87 \times 10^{10}\ \text{m}^{-1}$$

In units of Å, this value is 1.87 Å^{-1}. Its magnitude is understandable considering that in the course of a molecular vibration, the change in bond distance is on the order of ~0.1Å.

D_e is the dissociation energy with respect to the bottom of the potential energy curve. However, this is not what is measured experimentally, since molecules have a zero-point vibrational energy even at absolute zero. The energy that it actually takes to dissociate a diatomic molecule is determined from the $v = 0$ vibrational level, which has an energy of $\frac{1}{2}h\nu$ higher than the potential energy minimum. This amount of dissociation energy is labeled D_0 (the zero subscript is used as a reminder that this measurement is made with respect to the $v = 0$ vibrational state). The relationship between D_e and D_0, for diatomic molecules, is

$$D_e = D_0 + \tfrac{1}{2}h\nu \tag{14.38}$$

For polyatomic molecules, a factor of $\frac{1}{2}h\nu$ from all vibrations must be taken into account. Since there are $3N - 6$ vibrations in a (nonlinear) polyatomic molecule, the relationship between D_e and D_0 has a sum of $3N - 6$ terms:

$$D_e = D_0 + \sum_{i=1}^{3N-6} \tfrac{1}{2}h\nu_i$$

where the sum is over the $3N - 6$ (or $3N - 5$ for linear molecules) vibrations of the polyatomic molecule.

There is no theoretical basis for a Morse potential energy curve. Its form is empirical (that is, based on observation), but it is useful. First, it shows a dissociation limit, just as real diatomic molecules experience. The dissociation energy, D_e, appears in two places in the form of the Morse potential, as a premultiplicative term and as part of the definition of the constant a. It accurately predicts the observed trend of closer-spaced vibrational levels as the vibrational quantum number increases. Although diatomic molecules (and larger molecules also) do not behave as perfect Morse oscillators, the Morse potential is usually a better fit to the real vibrational behavior of molecules.

But the form of the Morse potential also allows us to quantify the amount of nonharmonic behavior of the molecule, or its *anharmonicity*. Because of its form, a system whose potential energy is expressed in terms of a Morse potential has a Hamiltonian that is solvable analytically. (It is one of the few solvable systems that we did not cover in Chapter 12.*) One finds that the energy of an oscillator having a Morse potential is quantized (no surprise here) and has values given by

$$E = h\nu_e(v + \tfrac{1}{2}) - h\nu_e x_e(v + \tfrac{1}{2})^2 \tag{14.39}$$

where ν_e is the *harmonic* vibrational frequency (*not* equal to ν of the classical harmonic oscillator!), v is the vibrational quantum number, and x_e is a dimensionless constant called the *anharmonicity constant*. Usually it is a small number. The smaller the number, the less anharmonic the oscillator is. The anharmonicity x_e is usually so small that in tabulations of anharmonicity data, not just x_e but $x_e \times \nu_e$ (sometimes written $\nu_e x_e$) is tabulated, usually in units of cm^{-1}. The deviation from the ideal harmonic oscillator energy is related to the *square* of the vibrational quantum number.

As part of the solution to the Schrödinger equation, the anharmonicity constant appears as a combination of other constants about the vibration. It is defined as

$$x_e = \frac{\nu_e}{4D_e} \tag{14.40}$$

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*In case you're curious, the wavefunctions for an oscillator that has a Morse-type potential energy function are

$$\Psi_n = N_n \cdot e^{t/2} \cdot t^{\alpha} \cdot \xi_n(t)$$

where N_n is a normalization constant, $t = Ke^{-ax}$, $K = (8\mu D_e/\hbar^2 a^2)^{1/2}$, and $\xi_n(t)$ is a polynomial function of t and K whose degree depends on the quantum number n. Compare this with the eigenfunctions for the harmonic oscillator from Chapter 11.

where the units on ν_e and D_e are the same so that x_e is unitless. Definition of a diatomic molecule as a Morse potential oscillator is useful because it ties in several important observables about that oscillator: classical frequency, dissociation energy, force constant, anharmonicity. Such relationships are complex but increase our understanding of the behaviors of such molecules. Table 14.4 also includes information on the anharmonicities of the various diatomic molecules.

Example 14.16

Predict where the $v = 0 \rightarrow v = 6$ transition for HCl will occur if it acts as an ideal Morse oscillator. Use the information in Table 14.4.

Solution

Using equation 14.39, we can calculate the following energies for the $v = 0$ and $v = 6$ vibrational energy states:

$$E(v = 0) = h\nu_e(0 + \tfrac{1}{2}) - h\nu_e x_e(0 + \tfrac{1}{2})^2$$

$$= (6.626 \times 10^{-34}\ \text{J}\cdot\text{s})(2989.74\ \text{cm}^{-1})(2.9979 \times 10^{10}\ \text{cm/s})(\tfrac{1}{2}) - (6.626 \times 10^{-34}\ \text{J}\cdot\text{s})(52.05\ \text{cm}^{-1})(2.9979 \times 10^{10}\ \text{cm/s})(\tfrac{1}{2})^2$$

$$E(v = 0) = 2.94 \times 10^{-20}\ \text{J}$$

The term 2.9979×10^{10} cm/s is the conversion directly from wavenumber (cm^{-1}) to frequency (s^{-1}). For $E(v = 6)$, similarly:

$$E(v = 6) = 3.42 \times 10^{-19}\ \text{J}$$

The difference in energy between the two vibrational states is 3.13×10^{-19} J; using the conversions $E = h\nu$ and $c = \lambda\nu$ and converting to wavenumber, this is equal to a transition occurring at 15,753 cm^{-1}. This is consistent with the trend of overtone absorptions in Table 14.3.

Diatomic molecules have a relatively simple vibrational spectrum because they have only one type of vibrational motion: a stretching motion. For linear triatomic molecules, the number of vibrations is four [$3N - 5 = 3(3) - 5 = 4$], which is three more than a diatomic molecule. The descriptions of the normal modes of vibration start getting a little more complicated. This is because for a normal mode, *the center of mass of the molecule does not move.* This means that all of the atoms in the molecule participate in each normal mode so that the center of mass stays fixed. Ultimately, this implies a more complicated exact description of the vibrational motion.

Although the exact description may be more complicated, an approximate description is often utilized in vibrational spectroscopy. Figure 14.30 shows the normal modes of vibration for linear triatomic molecules that are symmetric (such as CO_2) and asymmetric (such as HCN). Although the sets of normal modes are labeled similarly, using subscripts on the Greek letter ν to label the vibrations, the vibrations themselves are not described similarly. For the symmetric triatomic molecule, the vibration labeled ν_1 has the outside atoms moving in and out at the same time with respect to the center atom. Thus no overall change occurs in the dipole moment during this vibration and it is not considered *IR-active*; it is *IR-inactive*. This motion is called a *symmetric stretching vibration* (because both sides move symmetrically). The vibration labeled ν_3 is also a stretching vibration, but now the two outside atoms are moving one

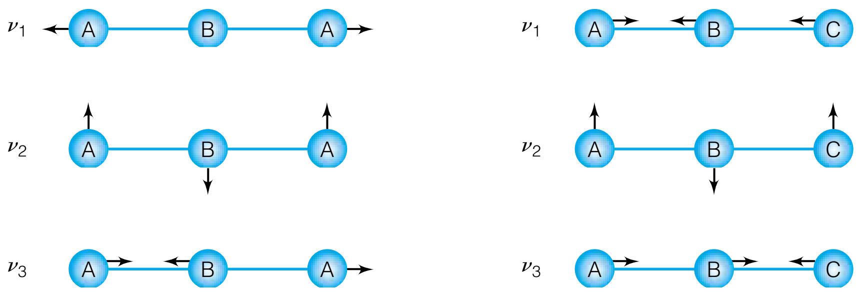

Figure 14.30 Normal modes of vibration for symmetric (ABA) and asymmetric (ABC) linear triatomic molecules. In both cases, the vibrations labeled ν_2 are doubly degenerate, since there are two equivalent vibrations that are perpendicular to each other. For the symmetric molecule, only ν_2 is IR-active. For the ABC molecule, all three vibrations are IR-active.

in, one out with respect to the center atom. This type of motion is called an *asymmetric stretching vibration.* It is IR-active, because a small dipole moment is produced during the course of the vibration (where the outside atoms are different distances from the center). Finally, the vibration labeled ν_2 has the center atom moving up-and-down while the outside atoms are moving down-and-up. The normally linear molecule becomes slightly bent during the course of this motion, and so this is called a bending motion. It, too, is IR-active: the molecule becomes bent and the overall dipole moment is no longer eliminated by symmetry. The interesting thing about this motion is that the bend can be either up-and-down or in-and-out, two directions that are 90° apart. These motions are perpendicular to each other and so represent a pair of *doubly degenerate* vibrational modes. They have the same frequency of vibration, and the same irreducible representation label. CO_2 is said to have a doubly degenerate bending motion (IR-active), a symmetric C–O stretching motion (IR-inactive), and an asymmetric C–O stretching motion (IR-active).

The asymmetric triatomic linear molecule also has a doubly degenerate bending motion labeled ν_2. (The numbering of the normal modes follows a system we won't get into here.) The other two motions correspond roughly to a stretching vibration between the left outside atom and the center atom, as well as a stretching vibration between the right outside atom and the center atom. So for HCN, we will have a doubly degenerate bending motion, and then two modes that are roughly described as an H–C stretching vibration and a C–N stretching vibration.

Because this one vibration is doubly degenerate, it must be counted twice in the summation that relates D_0 and D_e for polyatomic molecules. In larger molecules, degenerate vibrations must be summed the appropriate number of times to get the correct numerical relationship between D_0 and D_e.

Example 14.17

Roughly describe the four normal modes of the following linear molecules.

a. Carbon disulfide, CS_2

b. Hydrogen hypochlorite, HClO

c. Beryllium fluoride, BeF_2

d. The ethynyl radical, HCC·

Solution

a. CS_2 has a symmetric C–S stretch, an asymmetric C–S stretch, and a doubly degenerate bending motion.

b. HClO has, roughly, an H–Cl stretch, a Cl–O stretch, and a doubly degenerate bending motion.
c. BeF_2 has a symmetric Be–F stretch, an asymmetric Be–F stretch, and a doubly degenerate bending motion.
d. HCC· would be expected to have an H–C stretch, a doubly degenerate H–C–C bend, and a C–C stretching vibration.

Keep in mind that these descriptions are rough, not exact. Each atom in the molecule moves. This point gets lost when one begins to consider larger molecules, but it is no less true for simple triatomic molecules. Notice that we have introduced another type of vibrational motion: the bending motion. Such a motion does not fit the classical definition of a Hooke's-law system, which assumes that two masses are moving back and forth with respect to each other. However, even for bending motions, the case is made that the atoms are moving back and forth about some presumed equilibrium position. As such, we can assume some sort of force constant such that the farther away the atoms are from that equilibrium position, the stronger the restoring force. Therefore, *bending force constants* can be defined. However, in a bending motion, the concept of reduced mass of the oscillator is much more complicated. Bending motions in molecules therefore do not follow such simple mathematical relationships as do stretching motions, which were illustrated in Examples 14.12 and 14.13. (They do follow mathematical relationships, but they are a little more complicated. See G. Herzberg, *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules,* Van Nostrand Reinhold, New York, 1945.) For example, whereas the O–H and O–D stretches in H_2O are predicted in Example 14.13 to have a frequency ratio of about 0.73, which corresponds to the square root of the reduced mass ratio of the O–H and O–D bonds, the C–O–H bending motions of CH_3OH and CH_3OD have a frequency ratio of about 0.64, which is substantially less than the O–H/O–D reduced mass ratio.

Other linear molecules (acetylene, C_2H_2, for example) have similarly described vibrational spectra: either stretching vibrations or bending vibrations. It is only when a molecule becomes nonlinear that additional complexities arise. Unfortunately, most molecules are nonlinear. Fortunately, similar rough descriptions of the vibrations can be applied. Also fortunately, symmetry considerations combine with the change-in-dipole-moment selection rule to limit the number of IR-active vibrational motions of large, symmetric molecules. The next few sections will illustrate some of the procedures used to simplify our understanding of molecular vibrations.

14.13 Symmetry Considerations for Vibrations

A brief aside into symmetry is useful here. Recall that all molecules can be assigned a point group describing the symmetric arrangement (if any) of their atoms. This assumes, however, that the atoms are fixed in space. The very thought of vibrations suggests that the atoms are not fixed, and that specific symmetry designations are useless because the atoms are constantly moving around. Does this mean that vibrations of molecules destroy the symmetry of a molecule and that symmetry is not as applicable to molecules as we thought? No, it doesn't mean that. All normal modes of a molecule oscillate about an equilibrium position, and the *average* geometry of a molecule is defined in

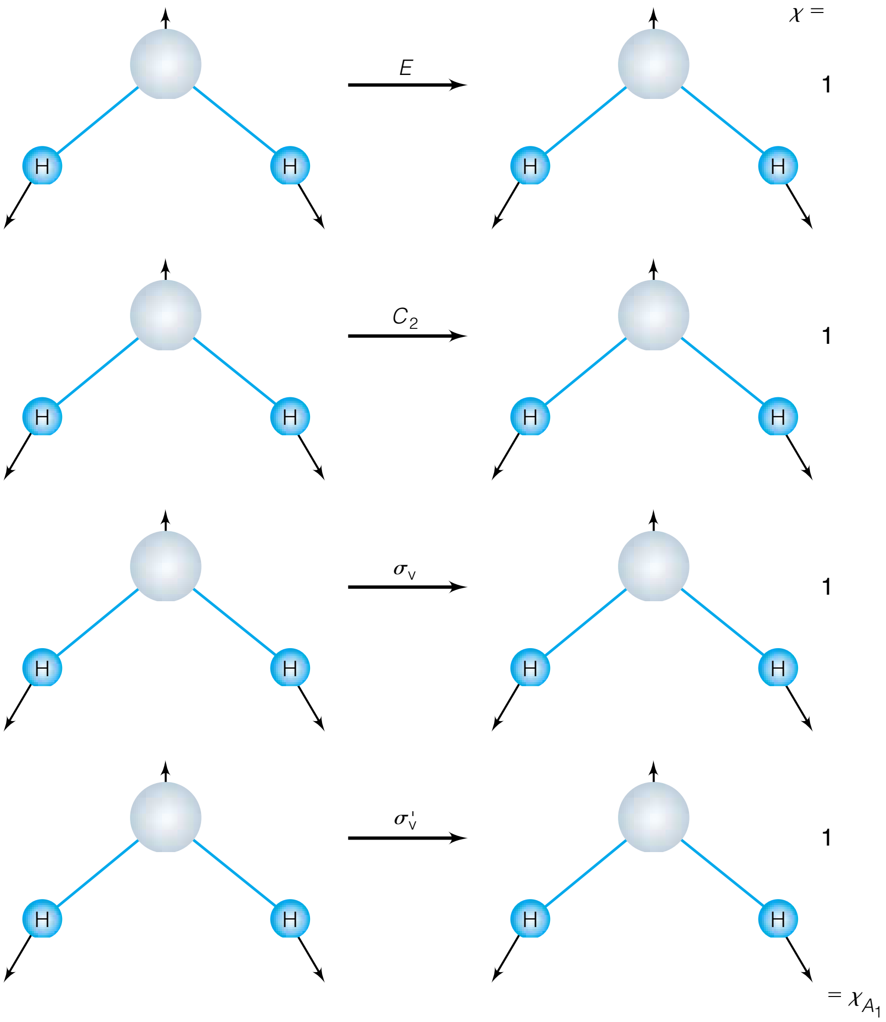

Figure 14.31 The ν_1 normal vibration of H_2O, and the effects of the symmetry elements of the C_{2v} point group on the vibration. In this case, operation of all symmetry elements yields a motion that is exactly the same as the original motion. Therefore, the eigenvalues of the operations are all 1, and this vibration can be labeled with the A_1 irreducible representation of the C_{2v} point group.

terms of these equilibrium positions. When we realize that (in most cases) the amount of movement of atoms in a vibration is relatively small, distorting a molecule very little from its equilibrium symmetry, the definition of a molecule as having a symmetry based on its equilibrium atomic positions is still a good basis for understanding its behavior.

Consider the vectors that describe the normal vibrations for the H_2O molecule in Figure 14.31, and the effects on those vectors by the various symmetry elements of the point group of the molecule, C_{2v}. The table on the right side of the figure shows that the group of eigenvalues produced for the vectors that describe the ν_1 vibration is the same as the irreducible representation A_1 for the point group. Inspection of the other normal vibrations shows that this is not a coincidence: the other two normal modes behave like irreducible representations of the C_{2v} point group also (A_1 and B_1, to be exact). Although proof is beyond our scope, the point should be clear: vibrational modes of molecules can be assigned a label of one of the irreducible representations of the molecular point group. The powerful mathematical tools of symmetry and group theory are therefore applicable to the study of molecular vibrations. We will use such tools to some extent in the material to come. Group theory is also applicable to other forms of spectroscopy, as we will find.

Example 14.18

From the representation of the normal modes of a symmetric linear molecule shown in Figure 14.30, draw the changes in the vectors upon operation of each symmetry element and assign irreducible representation labels to the normal modes of CO_2. You will have to use the $D_{\infty\text{h}}$ character table in Appendix 3.

Solution

The drawing is left to the student. If the drawings are done properly, it can be seen that the symmetric stretching vibration can be assigned a label of Σ_g^+; the asymmetric stretching vibration is assigned to Σ_u^+. The doubly degenerate bending motion is Π_u.

The degeneracy of a vibration is related to its character of the identity element of its irreducible representation label. Doubly degenerate vibrations always have an irreducible representation label having $\chi_E = 2$. Triply degenerate vibrations always have an irreducible representation label having $\chi_E = 3$. There are no higher degeneracies for vibrations.

14.14 Vibrational Spectroscopy of Nonlinear Molecules

Moving on to nonlinear molecules, there are few truly new concepts. The number of vibrational degrees of freedom is now $3N - 6$, and the list of descriptions for the vibrations increases somewhat. Perhaps the biggest difference in considering nonlinear molecules is how the symmetry of the molecule affects the number of independent vibrations of the molecule.

Figure 14.32 shows the normal vibrations for the ammonia molecule. They are numbered ν_1, ν_2, ν_3, and ν_4. The numbering of the vibrations follows a

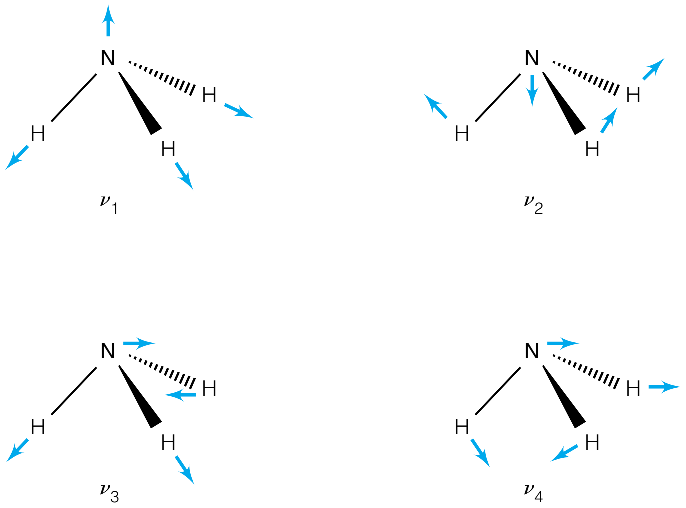

Figure 14.32 The normal modes of vibration for ammonia, NH_3. All are IR-active.

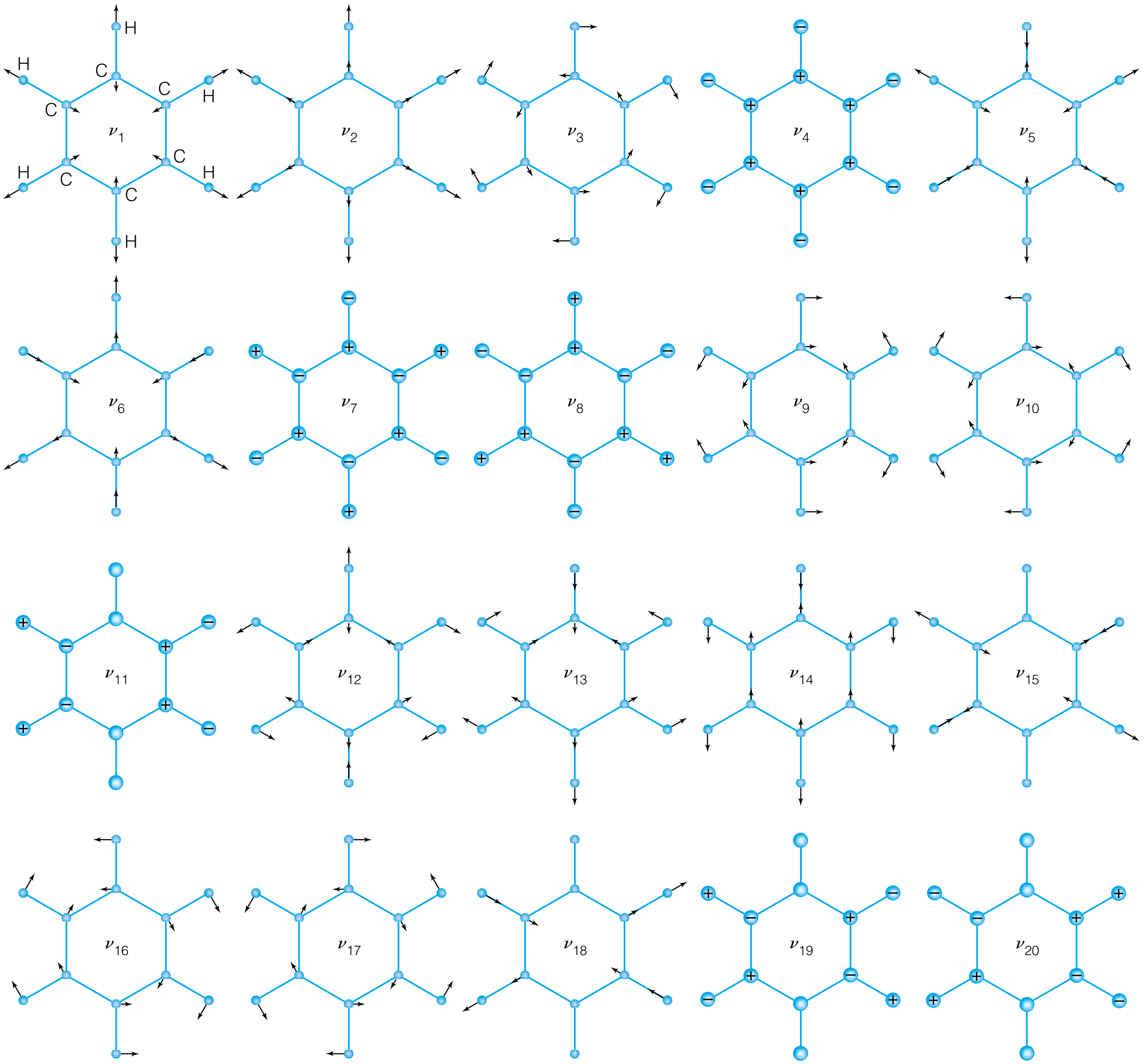

Figure 14.33 The normal modes of vibration for benzene, C_6H_6. Due to the high symmetry of benzene, only four of these vibrations are IR-active. *Source:* Gerhard Herzberg, *Molecular Spectra and Molecular Structure, Vol. II,* 1991, Krieger Publishing Company. Adapted with permission.

system that is recognized by spectroscopists. All are IR-active, so ammonia will absorb infrared radiation having four characteristic frequencies.

Figure 14.33 shows the normal vibrations for benzene, C_6H_6. For benzene, $3N - 6$ equals 30, so we expect to have up to 30 different vibrations. Some of the vibrations are degenerate, so there are less than 30 separate vibrations. However, *only four* vibrations are IR-active, since only four of them involve a changing dipole moment. (With respect to Figure 14.33, the IR-active vibrations are ν_4, ν_{12}, ν_{13}, and ν_{14}.) This is possible because the benzene molecule has many symmetry elements. Generally speaking, the higher the symmetry of the molecule, the fewer unique vibrational frequencies a molecule has, and the fewer that have a corresponding change in dipole moment.

There is a strict group-theoretical method for determining exactly the number of allowed vibrational transitions expected to be observed in a vibrational spectrum. The method is presented here as a sort of recipe to be followed, and uses the character tables in Appendix 3. Use of the recipe requires two things. First, the character tables contain more information than we have used so far. In particular, note the information in the rightmost column of the character tables. One or more of the irreducible representations of each character table has an x, y, or z notation at the right (among other things). These mark the irreducible representation(s) of the components of the electric dipole operator (see equation 14.2) in that particular symmetry. This information will be necessary in our recipe. Second, we need to differentiate between "proper" and "improper" rotations. In a broad sense, all symmetry operations can be thought of as rotations. Proper rotations are E and C_n, which have angles of rotation of 0° and 360°/n, respectively. Improper rotations are i, S_n, and all planes of symmetry; these have angles of rotation of 180°, 360°/n, and 180°, respectively. Proper and improper rotations are treated slightly differently in two steps of the recipe.

The recipe for determining the number of IR-active vibrations of a molecule of known symmetry is given in Table 14.5, in a somewhat abbreviated fashion. Briefly, it rests on finding a set of characters that describe the vibrational degrees of freedom of a molecule, then using the great orthogonality theorem to reduce that set of characters into a set of irreducible representations of the molecule's symmetry group. Then, by finding the x, y, and z labels in the character table, we can determine which irreducible representation labels correspond to vibrations that are infrared-active. The following example goes through the steps in the scheme.

Table 14.5 Steps for determining the number of infrared-active vibrations of a polyatomic molecule

Procedure	Formula/expression
Construct a blank table with a column for every symmetry class. In successive lines of the table, do the following:	
1. In the first line, write the number of atoms in the molecule that do not change their position in space under that operation.	$N_{\text{stationary}}$
2. In the next line, determine the angle θ of the "rotation" of the symmetry operation.[a]	θ
3. Evaluate the expression $(1 + 2\cos\theta)$ for each symmetry operation.	$(1 + 2\cos\theta)$
4. Evaluate $N_{\text{stationary}} \times (1 + 2\cos\theta)$, and multiply by $+1$ for proper rotations or -1 for improper rotations[b]. This is χ_{tot}.	$\pm N_{\text{stationary}} \cdot (1 + 2\cos\theta)$
5. Evaluate the character for rotations, χ_r, as $(1 + 2\cos\theta)$.	$\chi_r = (1 + 2\cos\theta)$
6. Evaluate the character for translations, χ_t, as $\pm(1 + 2\cos\theta)$ (depending on whether the operation is proper or improper).	$\chi_t = \pm(1 + 2\cos\theta)$
7. Subtract χ_t and χ_r from χ_{tot} to get the character set for vibrations, χ_v.	$\chi_v = \chi_{\text{tot}} - \chi_t - \chi_r$
8. Reduce χ_v into its irreducible representations using the GOT.	$\chi_v = \Sigma\Gamma_n$
9. Irreducible representations having x, y, or z labels in character table are IR-active.	

[a] For i, $\theta = 0°$. For S_3, $\theta = 60°$. For S_4, $\theta = 90°$. For S_6, $\theta = 120°$.

[b] Proper rotations are E and C_n; improper rotations are σ, i, and S_n.

Example 14.19

Determine the number of IR-active vibrations of carbon tetrachloride, CCl_4, which has T_d symmetry.

Solution

The steps and symbols are taken from Table 14.5. First, we construct a table by listing the classes of the symmetry operations in T_d symmetry:

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$

1. Determine $N_{stationary}$ for each symmetry class. You should verify that the following numbers are correct, as this is typically the most challenging part of the process.

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$N_{stationary}$	5	2	1	1	3

2. Determine the angle of rotation for all symmetry classes:

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$N_{stationary}$	5	2	1	1	3
θ	0°	120°	180°	90°	180°

3. Evaluate $(1 + 2\cos\theta)$:

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$N_{stationary}$	5	2	1	1	3
θ	0°	120°	180°	90°	180°
$1 + 2\cos\theta$	3	0	−1	1	1

4. Determine $\pm N_{stationary}(1 + 2\cos\theta)$, depending on whether the symmetry operation is considered a proper rotation or an improper rotation:

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$N_{stationary}$	5	2	1	1	3
θ	0°	120°	180°	90°	180°
$1 + 2\cos\theta$	3	0	−1	1	1
$\pm N_{stationary}(1 + 2\cos\theta)$	15	0	−1	−1	−3

5. Determine $\chi_r = 1 + 2\cos\theta$ for each symmetry class:

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$N_{stationary}$	5	2	1	1	3
θ	0°	120°	180°	90°	180°
$1 + 2\cos\theta$	3	0	−1	1	1
$\pm N_{stationary}(1 + 2\cos\theta)$	15	0	−1	−1	−3
χ_r	3	0	−1	1	1

6. Determine $\chi_t = \pm(1 + 2\cos\theta)$ for each symmetry class (again, depending on whether it is a proper or an improper rotation):

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$N_{\text{stationary}}$	5	2	1	1	3
θ	0°	120°	180°	90°	180°
$1 + 2 \cos \theta$	3	0	-1	1	1
$\pm N_{\text{stationary}}(1 + 2 \cos \theta)$	15	0	-1	-1	-3
χ_r	3	0	-1	1	1
χ_t	3	0	-1	-1	-1

7. Subtract χ_r and χ_t from χ_{tot} to get χ_v:

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$N_{\text{stationary}}$	5	2	1	1	3
θ	0°	120°	180°	90°	180°
$1 + 2 \cos \theta$	3	0	-1	1	-1
$\pm N_{\text{stationary}}(1 + 2 \cos \theta)$	15	0	-1	-1	3
χ_r	3	0	-1	1	1
χ_t	3	0	-1	-1	-1
χ_v	9	0	1	-1	3

8. Use the great orthogonality theorem to reduce χ_v into its irreducible representations for the T_d point group. Upon doing so (and the details are left to you), one finds that

$$\Gamma = 1A_1 \oplus 1E \oplus 2T_2$$

9. Check the T_d character table in Appendix 3. In the rightmost column, the T_2 irreducible representation has the x, y, and z labels. Therefore, only the T_2-labeled vibrations will be IR-active, and the conclusion is that CCl_4 will have only two IR-active vibrational modes. These modes, being triply degenerate, represent six of the nine normal vibrations of CCl_4.

The above example illustrates two things. First, the vibrational spectrum of a molecule can be enormously simplified because of symmetry. The nine possible (and presumably different) normal vibrations of CCl_4 are reduced to *only two* IR-active, triply degenerate vibrations. When you measure a vibrational spectrum of CCl_4, you will expect only two absorptions to appear in the spectrum instead of nine. Second, the use of group theory and character tables is indispensable in quantifying this. Group theory and symmetry are crucial to the understanding of vibrational spectroscopy in particular and all of spectroscopy in general. Although this is the first time we utilize the power of symmetry for a specific spectroscopic purpose, it should be understood that symmetry considerations and group-theoretical arguments are a fundamental aspect of spectroscopy.

The majority of molecules have relatively low symmetry, so they can be expected to have a large number of IR-active vibrations. However, this section has introduced a powerful concept that can be very useful in spectroscopy, especially in understanding how the structure of a molecule is related to its vibrational spectrum.

14.15 Nonallowed and Nonfundamental Vibrational Transitions

Because molecules are not perfect harmonic oscillators, the strict selection rules are not followed perfectly. In some cases $\Delta v = 2, 3, 4, \ldots$. These transitions are usually much weaker than for $\Delta v = 1$. In many cases, very bright light sources like lasers must be used to detect these transitions.

Overtone absorptions can be thought of as two or more vibrational quantum number steps. These are occasionally written in terms of the vibration number, for example $2\nu_3$ or $2\nu_{10}$ to indicate that the vibrational quantum number for ν_3 or ν_{10} of a particular molecule changes by 2. Although also forbidden formally, it is not unusual to find absorptions in a vibrational spectrum due to other combinations of the normal vibrations of the molecule. These are called *combination bands* and can be the addition of two (or more) normal vibrations of a molecule or even differences of two (or more) normal vibrations of a molecule. As might be expected, the larger the molecule, generally the greater the possibility of the appearance of combination bands. This is true because the larger the molecule, the less ideal it probably is.

For example, let us consider the vibrational spectrum of methylacetylene, $CH_3C{\equiv}CH$. The 15 normal vibrations reduce to 5 A_1-labeled motions and 5 E-labeled motions. Table 14.6 lists the 10 unique vibrational frequencies of methylacetylene. Also listed are other absorptions that are attributed to various overtones and combination bands. The nonideality of the molecule permits some of these combinations to appear with detectable intensity.

Table 14.6 also shows that, for the frequencies of the combination bands and overtones, the frequencies of the fundamental vibrations are not a perfect additive combination. This can make the assignment of combinations and overtones particularly tricky, especially for large molecules. Although there are symmetry rules for determining what vibrational frequencies will interact with what other vibrational frequencies, careful spectral studies using selective

Table 14.6 Infrared absorptions detected for methylacetylene

Normal vibration label	Symmetry species	Vibrational frequency
ν_1	A_1	3334.0
ν_2	A_1	2941.0
ν_3	A_1	2142.2
ν_4	A_1	Not observed
ν_5	A_1	930.7
ν_6	E	3008.3
ν_7	E	1452.0
ν_8	E	1052.5
ν_9	E	633.2
ν_{10}	E	328.0

Combination bands	Frequency
$\nu_3 + \nu_{10} - \nu_{10}$	2135.0
$\nu_3 + 2\nu_{10} - 2\nu_{10}$	2128.0
$\nu_5 + \nu_{10} - \nu_{10}$	932.2
$2\nu_9 + 2\nu_{10} - 2\nu_{10}$	1258.2
$2\nu_9 + \nu_{10} - \nu_{10}$	1256.8
$2\nu_9$	1255.0

[a] *Source:* D.R.J. Boyd, H. W. Thompson. *Trans. Farad. Soc.*, 1954, 50: 212.

isotopic substitution (for example, $CD_3C{\equiv}CH$ and $CH_3C{\equiv}CD$ for methylacetylene) is sometimes crucial in determining what normal vibrations contribute to combination bands.

14.16 Fingerprint Regions

Having spent the chapter discussing how vibrations of molecules absorb light of specific frequencies, we now introduce a useful generalization. Although a normal vibration involves all atoms in a molecule, in many instances a normal vibration is mostly due to a simple motion between two or three atoms in one part of the molecule. One consequence is that it is easy to describe normal motions by their majority component, like C–H stretch, O–H stretch, CH_2 wag, CH_3 deformation, or a similar description.

Another consequence is that all normal motions that can be given the same general description have similar vibrational energies. An equivalent way of stating this idea is that similar normal modes absorb infrared light from similar regions of the spectrum. That is, certain regions of the infrared spectrum correspond to characteristic types of vibrational motions of molecules. Such regions are called *group frequency regions* or *fingerprint regions,* and they typically refer to the fundamental vibration itself, not the overtones or combinations.

For example, the fingerprint region for an O–H stretch (say, for a series of different alcohol molecules) is about 3100–3800 cm^{-1}, depending on the specific molecule the O–H group is bonded to. Granted, this seems like a large range. However, it can be virtually guaranteed that such a motion will not be observed in the 100–500 cm^{-1} region. The masses of O and H are the same for all OH groups, and the force constant of the O–H bond does not change much with a change in the rest of the molecule. C–H stretches show up in the region 2800–3300 cm^{-1}. C–H bending motions appear in the 1300–1500 cm^{-1} and 500–900 cm^{-1} regions of the infrared spectrum. Other fingerprint regions can be identified. Table 14.7 lists several fingerprint regions that are useful in vibrational spectroscopy.

A more compact way than Table 14.6 to illustrate the fingerprint regions of various atomic combinations in molecules is the correlation tables. Correlation tables, like the one shown in Figure 14.34, can illustrate where certain groups of atoms will absorb in the vibrational spectrum. Additional correlation tables are shown in Appendix 4. These tables usually contain qualitative intensity information, allowing one to make judgments on the strength of an absorption in a vibrational spectrum. [In correlation tables, usually VS = very strong, S = strong, M = medium, W = weak, VW = very weak, SP or SH = sharp (that is, narrow), and BR = broad (that is, wide).] Correlation tables are useful for identifying compounds, because the right set of absorptions in the right fingerprint region(s) almost guarantees the presence of a certain grouping of atoms in a molecule. The following example illustrates.

Table 14.7 Various infrared fingerprint regions[a]

Motion type	IR region
C–H stretch	2800–3300
O–H stretch	3100–3800
C≡C, C≡N stretch	2100–2500
C=O stretch	1600–1800
C=C stretch	1600–1700
C–H bend	1300–1500, 500–900
O–H bend	1200–1600
C–O stretch	900–1300
C–C stretch	800–1150

[a] All units are cm^{-1}. Limits are approximate, since there are usually examples of molecules whose motions are outside the specified range.

Example 14.20

An unknown compound shows vibrational absorbances occurring at 3287, 2215, and 729 cm^{-1}. Keeping in mind that these are not all of the vibrational frequencies of the molecule, use the concepts of fingerprint regions and correlation tables to determine whether or not such absorptions are likely for the following molecules.

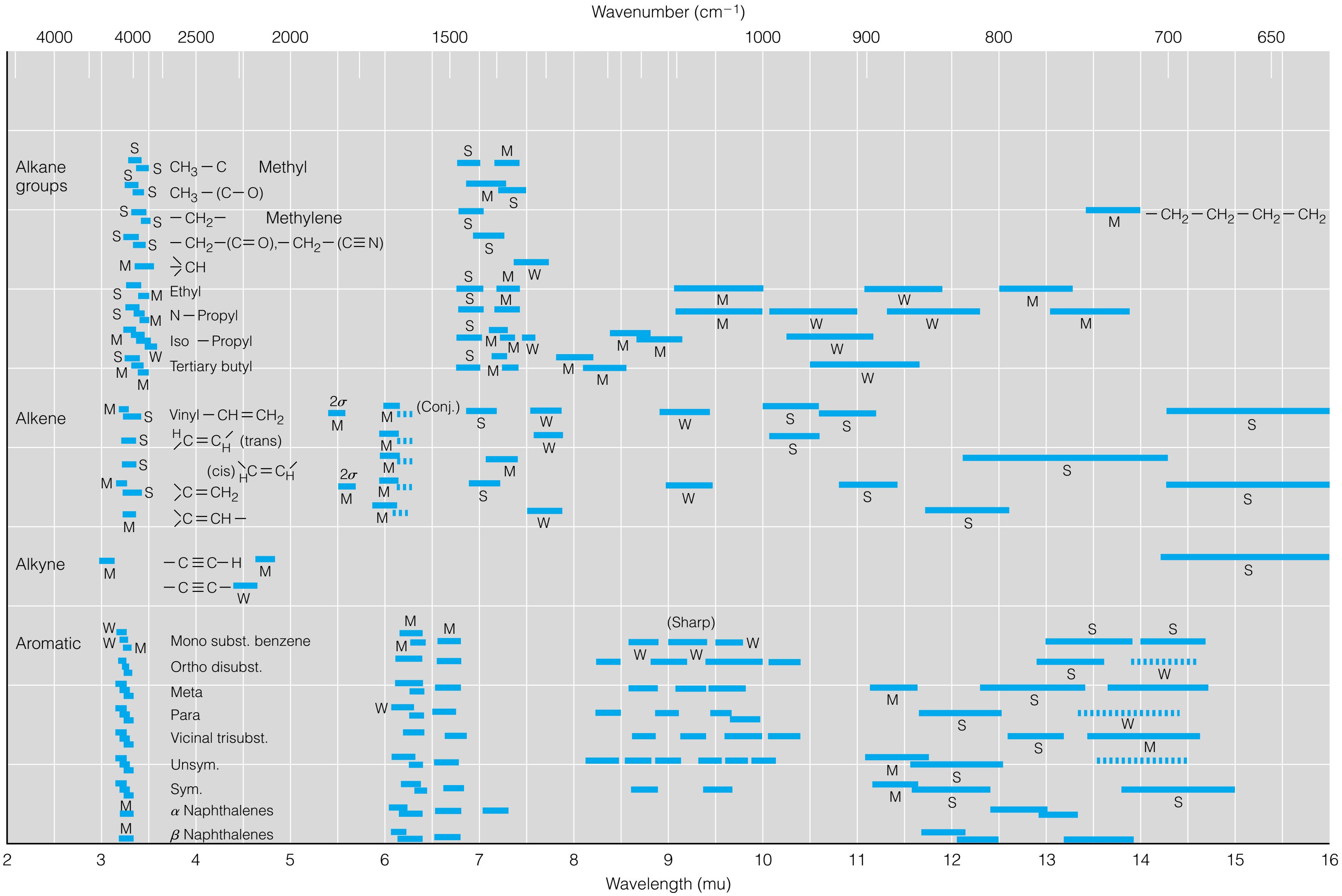

Figure 14.34 A correlation table for assigning infrared spectra. Tables like this are useful in trying to identify molecules from their vibrational spectrum.

a. Water, H_2O
b. Methane, CH_4
c. Acetylene, C_2H_2
d. Ethane, CH_3CH_3
e. Ethynol, $CH{\equiv}COH$ (that is, the alcohol made from acetylene, or ethyne)

Solution

a. Although the 3287 cm^{-1} absorption might be due to an O–H motion, neither of the other two absorptions correspond to any type of motion due to oxygen and hydrogen bonded together. Therefore, water is probably not a likely candidate to have this spectrum.
b. The correlation tables show an absorption in the range where 729 cm^{-1} would fall, but neither of the other two absorptions agree with the tables. (Although the 3287 cm^{-1} absorption might seem close, it seems high for an alkane. Too, the peak at 2215 cm^{-1} is not near any alkane fingerprint region.) Therefore, methane is not a likely candidate for such absorptions.
c. The 3287 cm^{-1} absorption is in the range of an alkyne C–H absorption. Further, the absorption at 729 cm^{-1} is close to the region where alkyne C–H bonds absorb (this is the C–H bending motion). Finally, the absorption at 2215 cm^{-1} falls in the range of C≡C vibrations. The conclusion is that this could represent a possible (partial) spectrum of acetylene.
d. As for methane, although the C–H fingerprint regions may be represented, there is no acceptable fingerprint region that could explain the absorption at 2215 cm^{-1}. Therefore, ethane is not a likely candidate for having these absorptions.
e. Although C–H vibrations and C≡C vibrations are represented (as with acetylene, above), there is no mention of an absorption for an O–H motion. Therefore, we make a qualified statement that these absorptions might describe this molecule, but we would need to check for the presence or absence of absorptions belonging to an O–H group. If such normally medium or strong absorptions are absent, then identification of the compound as ethynol might not be the best identification.

The last part of Example 14.20 illustrates a major pitfall in using correlation tables and fingerprint regions for understanding vibrational spectra. They help, certainly, but they do not *guarantee* identification. All substances have their own characteristic spectra, and a positive identification of a molecule rests on being able to match a vibrational spectrum exactly, or as closely as possible. Fingerprint regions and correlation tables provide clues and hints. But in almost all cases, that is all they provide. Nonetheless, they are useful in making general interpretations about the structure of a molecule on the basis of its vibrational spectrum. For small molecules, where group-theoretical analyses can also be applied, such tools are indispensable for identification of unknown molecules.

14.17 Rotational-Vibrational Spectroscopy

Although it is easier to discuss rotations and vibrations of molecules separately, in reality such motions of molecules occur simultaneously. (Translations are also occurring, and translational motion accounts for a large part of the kinetic energy of a molecule in the gas phase. However, translations do not contribute directly to the topic at hand.) When a sample is in the gas phase, molecules are unhindered in their rotational and vibrational motions, and so both occur simultaneously. In the liquid phase, vibrational motions occur relatively unhindered but rotational motions may be hindered. In the solid phase, vibrations are relatively hindered, and with a few exceptions the rotations are quenched.

A gas-phase sample undergoes vibrational and rotational motion. Vibrations typically absorb in a certain region of the spectrum, the infrared region. *Pure* rotational motions absorb energy in the microwave region of the spectrum, but the energy involved in a rotational state transition is not negligible compared to the vibrational energy. In the process of absorbing vibrational energy, many molecules can simultaneously undergo a rotational energy transition. Although the energy difference due to the vibrational state transition is constant (and equals $h\nu$), the energy difference due to rotational state transitions depends on the initial rotational quantum number J. Therefore, the combination—or *superposition*—of rotational transitions with a vibrational transition is also a series of absorptions. Such a series of absorptions, relatively regularly spaced, typifies *rotational-vibrational spectroscopy.* Sometimes the term *rovibrational spectroscopy* is used.

The spectrum of gaseous HCl is a classic example of rovibrational spectroscopy. An example of an HCl spectrum is shown in Figure 14.35. The series of absorptions is separated into two distinct regions. From 3100 to 2900 cm^{-1} is the combination rotational-vibrational change in quantum number ($\Delta\nu = +1$, $\Delta J = +1$), and from 2860 to 2600 cm^{-1} the quantum number changes are ($\Delta\nu = +1$, $\Delta J = -1$). For both regions, or *branches,* the change in the vibrational quantum number is $+1$, because in absorption spectroscopy the vibrational quantum number increases. Normally, in pure rotational absorption spectra, the change in the J quantum number is also $+1$. But when a molecule changes vibrational states, there is the possibility that the molecule can go to the next vibrational level but also simultaneously to a *lower value* for the J quantum number. Because going to a lower rotational state implies an overall loss of energy, the ($\Delta\nu = +1$, $\Delta J = -1$) transitions appear at lower energies

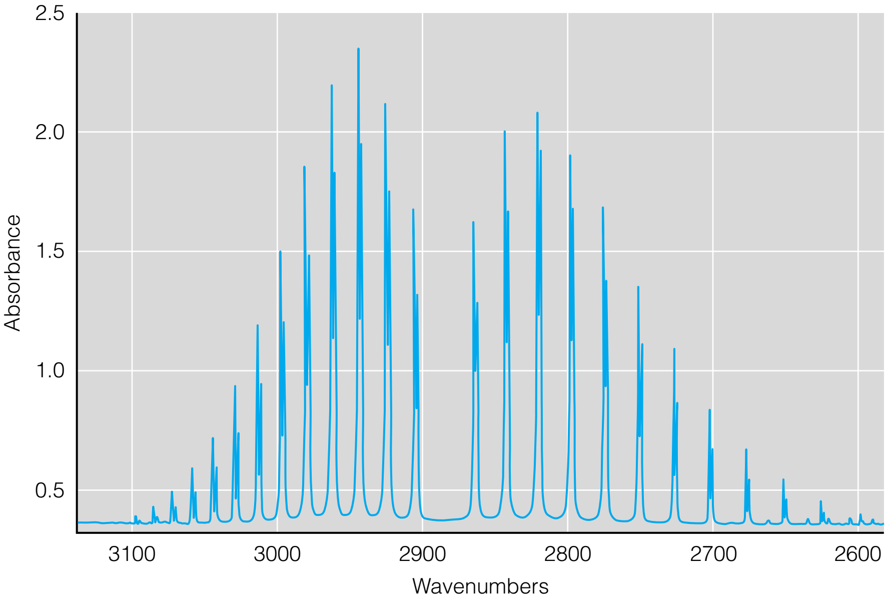

Figure 14.35 Complete P and R branches of the rovibrational spectrum of HCl gas. The doublet character of each absorption is due to the natural isotopic abundances of ^{35}Cl and ^{37}Cl.

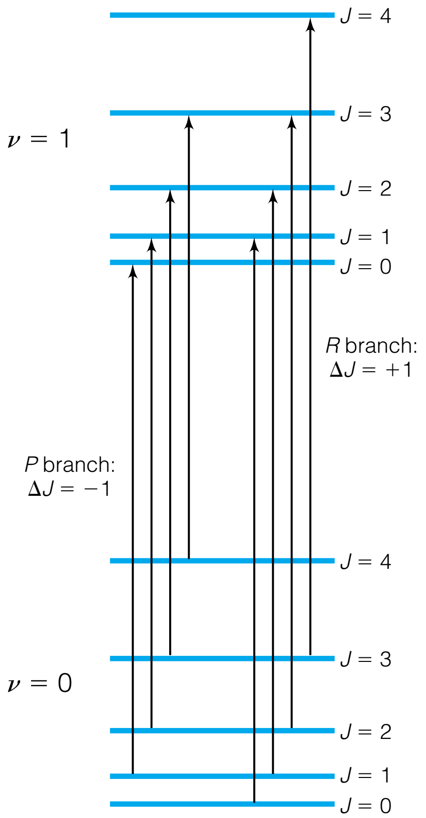

Figure 14.36 Energy-level diagram showing the origin of *P* and *R* branches in a rovibrational spectrum. For some molecules, a *Q* branch, in which $\Delta J = 0$, can also be seen.

than do the ($\Delta v = +1$, $\Delta J = +1$) transitions. All of the $\Delta J = +1$ transitions appear at higher energies than the pure vibrational transition (where ΔJ would be 0), and all of the $\Delta J = -1$ transitions appear at lower energies than the pure vibrational transition. The pure vibrational transition would fall in between the two branches. The branch where $\Delta J = -1$ is called the *P branch,* and the branch where $\Delta J = +1$ is called the *R branch.* Figure 14.35 shows *P* and *R* branches for the rovibrational spectrum of HCl gas. Figure 14.36 shows a diagram of the individual transitions in the rovibrational spectrum. In the *P* branch, it can be seen that the quantum number *J* decreases by 1 for each transition. In the *R* branch, *J* increases by 1.

Rotational spectra of linear molecules can be related to a rotational constant *B*, which in turn is related to the reduced mass and bond length of the molecule. In rovibrational spectra, the excited vibrational state does not necessarily have the same value for *B* as the ground rotational state. We therefore need to differentiate between B_0 and B_1 for the ground and excited vibrational states, respectively. Also, there are anharmonicity and centrifugal distortion effects (characterized by $x_e\nu_e$ and D_J constants, respectively) that will determine the exact wavelength of light that a rovibrational transition will absorb. Such effects account for (1) the difference in spacing between the absorptions of the *P* branch and the absorptions of the *R* branch, and (2) the small but observable change in the separation of the absorptions within each branch. You should be able to notice both effects in Figure 14.35. To a very good approximation, for diatomic molecules having rovibrational spectra, the lines in the fundamental vibration spectrum (that is, $v = 0 \rightarrow v = 1$) can be predicted by the following equations, which account for changes in v, J, B_0 and B_1, and the effects of anharmonicity and centrifugal distortion. For the *R* branch:

$$\Delta E = h\nu - 2x_e\nu_e + (B_1 + B_0)(J_{\text{lower}} + 1) + (B_1 - B_0)(J_{\text{lower}} + 1)^2 - 4D_J(J_{\text{lower}} + 1)^3 \tag{14.41}$$

and for the *P* branch:

$$\Delta E = h\nu - 2x_e\nu_e - (B_1 + B_0)J_{\text{lower}} + (B_1 - B_0)J_{\text{lower}}^2 + 4D_J J_{\text{lower}}^3 \tag{14.42}$$

where J_{lower} indicates that the equation uses the *J* value of the lower rotational-vibrational state. Notice the minor differences in signs and the terms in J_{lower} in the two equations. These differences are enough to be noticeable in some rovibrational spectra, like Figure 14.35. Although the above equations assume the $v = 0 \rightarrow v = 1$ fundamental vibrational transition, they do not assume any particular rotational state. Expressions like equations 14.41 and 14.42 are used to calculate anharmonicities, rotational constants, and so on from experimental spectra, since in most cases there are a lot of absorptions to fit to the equations. Much of the data in Tables 14.2 and 14.4 was determined this way.

There is such a thing as a *Q branch,* where the change in the *J* rotational quantum number is zero; that is, $\Delta J = 0$. With no change in *J*, the only effects on ΔE for the transition are vibrational, from the change in the harmonic vibrational frequency and the effects due to anharmonicity. *Q* branches are therefore much more compact than *P* or *R* branches. However, Figure 14.35 shows no visible *Q* branch (which would be expected to occur right between the *P* and *R* branches). Recall the selection rule given in equation 14.18, which is $\Delta J = \pm 1$: a ΔJ of 0 is usually forbidden, suggesting that *Q* branches will not be seen. This is true for most diatomic molecules. For polyatomic molecules, linear or nonlinear, *Q* branches may occur. However, there is no simple selection rule. Figure 14.37 shows the *P*, *Q*, and *R* branches for carbon dioxide, CO_2.

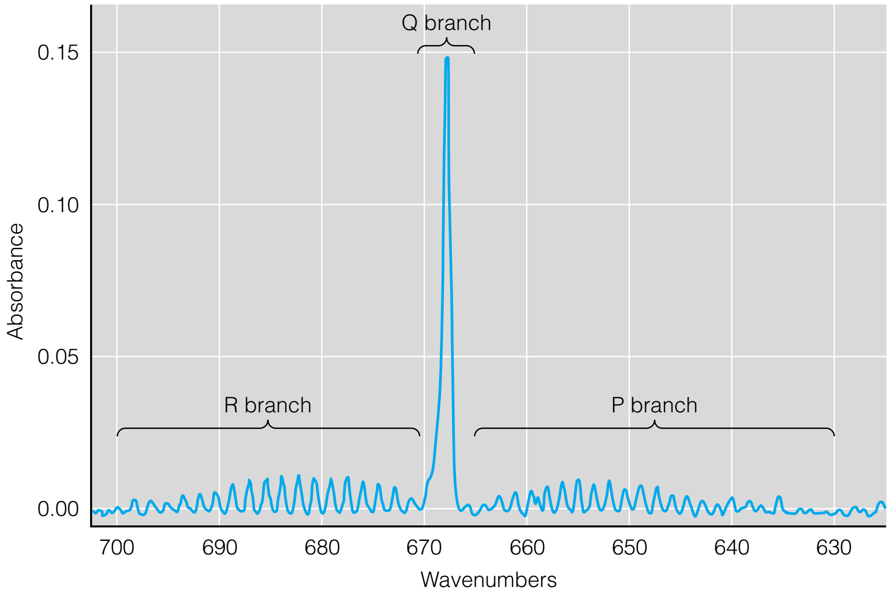

Figure 14.37 Rovibrational spectrum of CO_2, showing a *Q* branch.

Rovibrational spectra for nonlinear polyatomic molecules are more complicated. For polyatomic molecules that have a permanent dipole moment, there can be up to three *independent* rotational lines superimposed on a single normal vibration of the molecule. Figure 14.38 shows a rovibrational spectrum of H_2O in the gas phase, where the molecules can rotate freely. Even though we have increased the size of our molecular system by only one atom, the complexity of the spectrum has increased dramatically. But because of the large amount of molecular data that can be derived from such spectra, the detailed

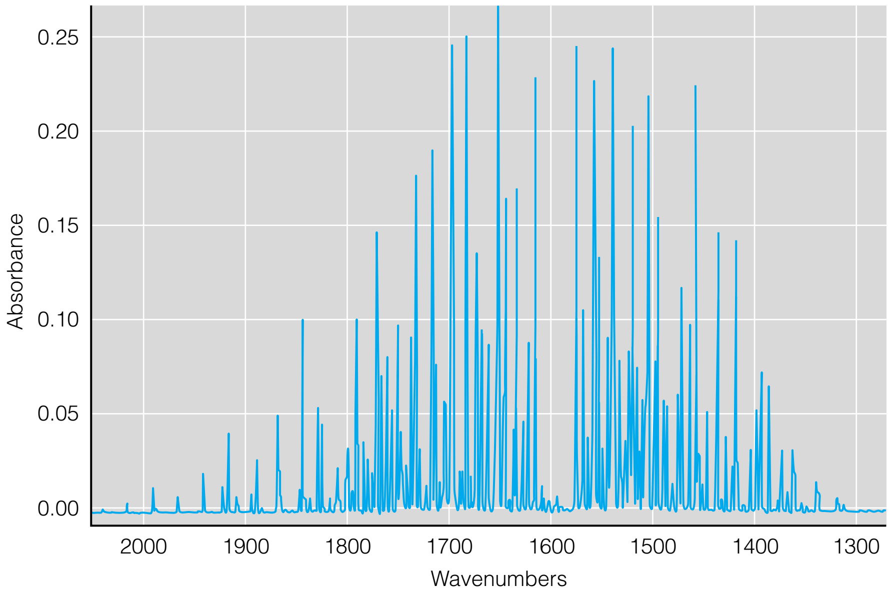

Figure 14.38 Part of the rovibrational spectrum of H_2O vapor. Compare this with Figure 14.37. Although both CO_2 and H_2O are triatomic, H_2O's spectrum is much more complicated than CO_2's because it is a nonlinear, asymmetric top molecule.

study of the rotational-vibrational spectra of nonlinear polyatomic molecules is as rewarding as it is complex.

Example 14.21

The peaks representing the R branch get closer and closer together as J increases. **a.** Use equation 14.41 to estimate at what rotational state the rovibrational lines will cease to be separated from each other, and will start moving to lower energy. (This point is called the *band head* of the series of absorptions.) To simplify the problem, neglect the centrifugal distortion term. Use $B_0 = 10.44\ \text{cm}^{-1}$ and $B_1 = 10.14\ \text{cm}^{-1}$.
b. What is the maximum populated rotational level of HCl at 298K? (Use equation 14.23.)
c. On the basis of the previous answer, would one expect to observe the band head in a spectrum measured at this temperature?

Solution

a. Using the expression from equation 14.41, the separation between two adjacent absorptions, labeled $\Delta(\Delta E)$, is independent of the harmonic vibrational frequency and the anharmonicity and is equal to

$$\Delta(\Delta E) = (B_1 + B_0) + (B_1 - B_0)(2J + 3)$$

where $\Delta(\Delta E)$ is the symbol for the difference between the ΔE values of the spectrum. Evaluating the sum and difference of the B values in the above expression:

$$\Delta(\Delta E) = 20.58\ \text{cm}^{-1} - 0.30(2J + 3)\ \text{cm}^{-1}$$

This separation is usually positive, since the first term normally overwhelms the second, negative term. However, at a high enough J value, the second term will cancel out the first term so that the lines in the spectrum will first overlap and then start progressing toward higher energies. We want the value of J where $\Delta(\Delta E)$ is about zero:

$$0 = 20.58\ \text{cm}^{-1} - 0.30(2J + 3)\ \text{cm}^{-1}$$

Solving for J algebraically yields

$$J = 32.8 \approx 33$$

for the approximate position of the band head.
b. Using

$$J_{\text{max}} \approx \left(\frac{kT}{2B}\right)^{1/2}$$

we will first have to convert one of the B values to appropriate units. We get

$$B = 10.44\ \text{cm}^{-1}\left(\frac{2.9979 \times 10^{10}\ \text{cm}}{\text{s}}\right)6.626 \times 10^{-34}\ \text{J·s} = 2.074 \times 10^{-22}\ \text{J}$$

where we have arbitrarily used the ground-state B_0. Substituting:

$$J_{\text{max}} \approx \left[\frac{(1.381 \times 10^{-23}\ \text{J/K})(298\text{K})}{2(2.074 \times 10^{-22}\ \text{J})}\right]^{1/2}$$

All of the units cancel, so that we are taking the square root of a unitless number. We get

$$J_{\text{max}} \approx 4.5$$

or equal to about $J = 4$ or 5. (How does this compare with the spectrum in Figure 14.35?)

c. Given that the band head occurs at around $J = 33$, we are 28 or so quantum rotational levels away. Since the spectrum in Figure 14.35 seems to diminish in intensity rather quickly, it is doubtful that the band head will be observed for this molecule at this temperature. Chances of observing it would be better if the temperature were increased. With the inclusion of the centrifugal distortion, however, the band head would be expected to occur at slightly lower *J*, but still not low enough to be observed at normal temperatures.

14.18 Raman Spectroscopy

When light is passed through a transparent sample, most of the light is transmitted through the sample. A tiny amount of light (about 1 photon in 10^4) is scattered from the sample at some angle and comes off at some angle. This light has the same frequency as the incoming light, and the extent to which light is scattered is inversely proportional to the fourth power of its wavelength.* This phenomenon is called *Rayleigh scattering*. Rayleigh scattering can be thought of as *elastic* collisions between molecules and photons.

An even smaller amount of light (about 1 photon in 10^7) is scattered but changes frequency: these can be thought of as inelastic collisions between molecules and photons. This phenomenon is called *Raman scattering*, after the Indian physicist Chandrasekhara Raman, who is credited with discovering the effect in 1928. Raman scattering is interesting because the energy changes of the outgoing photons correspond to changes in quantized energy levels of the molecules in the sample:

$$\Delta E(\text{photon}) = \Delta E(\text{energy levels}) \tag{14.43}$$

Thus, Raman scattering forms the basis for a type of spectroscopy, called *Raman spectroscopy*. Today, Raman spectroscopy is performed using lasers as the incoming light source because the laser light is intense (providing a better chance to observe photons that have shifted frequency) and monochromatic (making it easier to find shifted-frequency photons).†

Raman spectroscopy is used to study many different types of spectral transitions, but for our purposes we focus on the use of Raman scattering to study the vibrational energy transitions of molecules. Incoming photons will interact with molecules and, in a small number of cases, lose some of their energy to the vibrations of the molecules. The outgoing photons, scattered in all directions, will lose a small amount of energy equal to the difference in the vibrational energy levels of the molecule. From quantum mechanics, the energy difference between the incoming and outgoing photon equals the energy difference in the quantized vibrational energy levels:

$$\Delta E(\text{photon}) = h\nu_i \tag{14.44}$$

where ν_i is the classical frequency of the *i*th vibration of the molecule.

An example of a Raman spectrum of tetrafluoroethylene, C_2F_4, is shown in Figure 14.39. There are some differences between a Raman spectrum and an absorption vibrational spectrum. First, a Raman spectrum is a plot of the

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*Rayleigh scattering is reponsible for the blue color of the sky. Blue light scatters more than other wavelengths because of its shorter wavelength.

†Raman and his colleagues used sunlight and, later, mercury lamps as light sources.

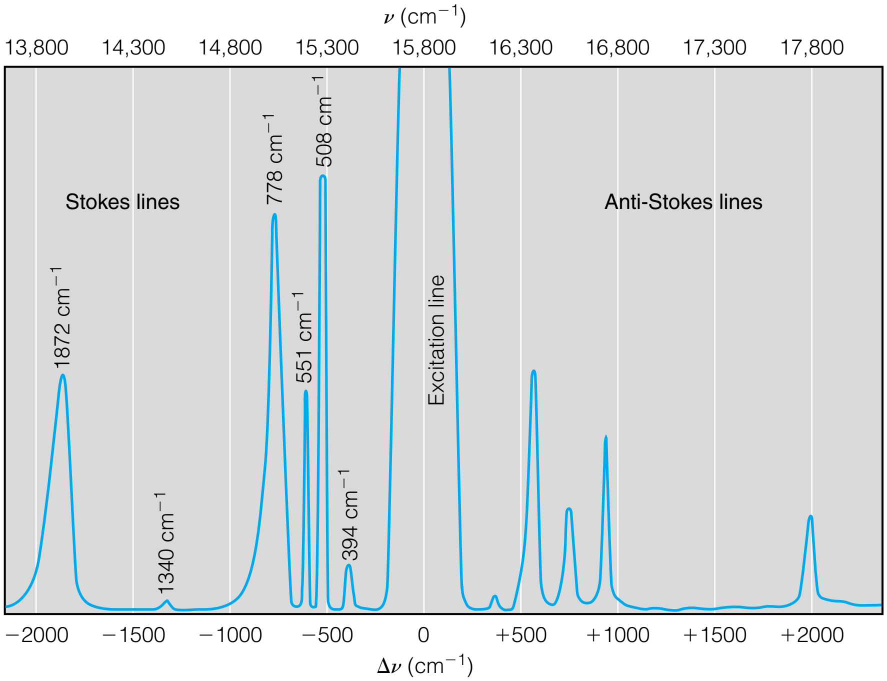


Figure 14.39 A Raman spectrum of tetrafluoroethylene, CF_2CF_2. The difference between the frequency of the emitted photon and the excitation photon equals an energy of vibration of the molecule. The Stokes lines and anti-Stokes lines are modified mirror images of each other, reflected through the excitation frequency. Anti-Stokes lines are always lower in intensity than the corresponding Stokes line.

energy *difference* between the incoming light and the outgoing light. Thus, if the incoming light is in the visible part of the spectrum, the outgoing light is also in the visible part of the spectrum. It's the *changes* in the energy of the photons that equal the vibrational energy differences (rather than the absolute energies of the photons). Figure 14.39 shows two scales on the abscissa of the spectrum, an absolute frequency of the light (which shows that the spectrum is being measured in the visible portion of the electromagnetic spectrum), and a difference in frequency of light (which shows magnitudes that are consistent with vibrations of molecules). A $\Delta\nu$ value of 0 is at the frequency of the incoming, excitation light—in this case, the 632.8-nm wavelength of the red light of a He-Ne laser. There is a very large peak at that position because of the relatively intense Rayleigh scattering of the incoming light. Some photons appear at lower frequencies, with the energy shifts corresponding to the vibrational frequencies of C_2F_4. Thus, this Raman spectrum is giving us a vibrational spectrum of the sample.

Another difference between Raman spectroscopy and regular absorption spectroscopy is that occasionally an outgoing photon *increases* its energy by interacting with a molecule that is energetically excited. In this circumstance, the photon increases its frequency and we see a spectrum on the higher-energy side of the excitation light. Because the same energy levels of the molecule are involved, we see the same—but reflected—vibrational spectrum we see on the lower-energy side of the excitation line, only less intense (because there are typically fewer molecules in the excited energy states). This is also shown in Figure 14.39. The lines of the spectrum on the lower-energy side are called the *Stokes lines*, and the lines of the spectrum on the higher-energy side are called the *anti-Stokes lines* (after George Gabriel Stokes, an Irish mathematician who discovered fluorescence in 1852).

Raman spectroscopy also has selection rules. The gross selection rule for a Raman-active vibration is related to the polarizability of the molecule. *Polarizability* is a measure of how easily an electric field can induce a dipole moment on an atom or molecule. Vibrations that are Raman-active have a changing polarizability during the course of the vibration. Thus, a changing polarizability is what makes a vibration Raman-active. The quantum-mechanical selection rule, in terms of the change in the vibrational quantum number, is based on a transition moment that is similar to the form of M in equation 14.2. For allowed Raman transitions, the transition moment $[\alpha]$ is written in terms of the polarizability α of the molecule:

$$[\alpha] = \int \Psi^*_{\text{final}} \alpha \Psi_{\text{initial}}\, d\tau \qquad \textbf{(14.45)}$$

where Ψ_{final} and Ψ_{initial} are the final and initial vibrational wavefunctions, respectively. As with vibrations absorbing infrared light, it can be shown that this integral is exactly zero unless the difference in the quantum numbers of Ψ_{final} and Ψ_{initial} is ± 1:

$$\Delta v = \pm 1 \quad \text{for allowed Raman vibrational transitions} \qquad \textbf{(14.46)}$$

IR-active vibrations require a changing dipole moment, which is relatively easy to visualize by inspection of the normal mode's atomic vectors. Changes in polarizability are not as straightforward to visualize. But, as with IR-active vibrations, we can use the great orthogonality theorem to determine the number of Raman-active vibrations that a molecule will have. The procedure is the same as what was done using Table 14.5 in Example 14.19, except for step 9, in which we use information in the character table to determine which irreducible representations are spectroscopically active. For IR-active vibrations, we looked for the x, y, and z labels on the irreducible representations. These labels gave us an indication of the irreducible representation of the dipole moment operator in those point groups. But according to equation 14.45, the operator for the Raman transition moment is α, not μ. The polarizability α has different irreducible representations in the point groups, and those irreducible representations are labeled with second-order variables: x^2, y^2, z^2, xy, yz, xz, or other combinations of second-order functions. Such functions are listed in the character tables in Appendix 3. Vibrations that have irreducible representations associated with these labels are Raman-active.

Example 14.22

Use the information in Example 14.19 to determine which vibrations of carbon tetrachloride, CCl_4, are Raman-active.

Solution

According to step 8 of Example 14.19, the vibrations of CCl_4 collectively have the irreducible representations

$$\Gamma = 1A_1 \oplus 1E \oplus 2T_2$$

If we check the T_d character table in Appendix 3, we find second-order functions listed with A_1, E, and T_2 irreducible representations. Therefore, all of the vibrations of CCl_4 will be Raman-active, and the Raman spectrum will consist of four signals representing one singly degenerate, one doubly degenerate, and two triply degenerate vibrations.

By comparing the solutions of Examples 14.19 and 14.22, we see that vibrational absorption spectroscopy and Raman spectroscopy provide different information. Absorption and Raman spectroscopies are *complementary* techniques. In fact, by comparing the results of absorption and Raman spectra and doing a group-theoretical analysis, one can provide evidence for or against a particular symmetry for a molecule. (See the end-of-chapter exercises for an example of this sort of analysis.) Raman spectra can provide additional information by analyzing the polarization differences between the incoming and outgoing light (another advantage of using lasers as a light source). Such analyses are beyond our scope; additional information can be found in more detailed texts about Raman spectroscopy.

Raman spectroscopy can be used to probe other energy levels besides vibrational. For example, rotational and electronic energy levels can also be investigated using Raman scattering. Raman spectroscopy is just one more tool in the modern chemist's arsenal for the study of atoms and molecules.

14.19 Summary

This chapter gives a brief introduction of rotational and vibrational spectroscopy. It is an enormously powerful subject when applied to the study of molecules. Performed and analyzed properly, a rotational or vibrational spectrum can yield direct information about the structure of a molecule. Pure rotational spectroscopy, which utilizes the microwave portion of the electromagnetic spectrum, allows us to calculate sizes of molecules that agree with the atomic scale assumed by Dalton's atomic theory. Microwave spectroscopy has also been useful in observing the universe around us. Astronomical observatories have identified specific molecules existing in interstellar space, like H_2O, HCN, H_2S, C_2H_2, even C_2H_5OH—all from microwave (that is, rotational) spectra observed by microwave "telescopes." Such knowledge supports the idea that the chemicals in our world exist not just here but throughout the universe.

Vibrational spectroscopy also provides valuable information about the structures of molecules, especially when one combines the complementary tools of infrared absorption and Raman spectroscopies. Vibrational spectra, coupled with group theory and symmetry, are indispensable tools for inferring the structure of a molecule, for determining how atoms in a molecule are bonded together. Fingerprint regions are also a quick method of establishing what groups of atoms exist in a molecule. Together, rotational and vibrational spectroscopy deal with the relative nuclear motions of molecules.

EXERCISES FOR CHAPTER 14

14.2 & 14.3 Selection Rules and Electromagnetic Light

14.1. Why won't a rotational spectrum be observed for the rotation of a linear molecule about its linear axis?

14.2. Determine if the following integrals can be nonzero if the molecular or atomic system has the given local symmetry. Use the great orthogonality theorem if necessary.

(a) $\int \Psi^*_{A_u} \widehat{O}_{B_{2u}} \Psi_{A_u}\, d\tau$ in D_{2h} symmetry

(b) $\int \Psi^*_{A_1} \widehat{O}_{A_1} \Psi_{A_2}\, d\tau$ in C_{3v} symmetry

(c) $\int \Psi^*_{\Sigma_g^+} \widehat{O}_{\Sigma_g^-} \Psi_{\Sigma_g^-}\, d\tau$ in $D_{\infty h}$ symmetry

(d) $\int \Psi^*_{E} \widehat{O}_{A_2} \Psi_{T_1}\, d\tau$ in T_d symmetry

14.3. What is the frequency of light having the following wavelengths? **(a)** 1.00 m **(b)** 4.77×10^{-5} m **(c)** 7894 Å **(d)** 1.903×10^{3} m

14.4. The $Cu(H_2O)_6{}^{2+}$ complex has octahedral symmetry. Is a transition from a T_{2g} state to an E_g state allowed if the transition moment operator has a T_{1u} symmetry label?

14.5. What are the wavelength, speed, and energy of a photon that has a frequency of $8.041 \times 10^{12}\ s^{-1}$?

14.6. Show that the wavenumber of any electromagnetic light is proportional to its frequency.

14.7. Both of the units micron (wavelength) and cm^{-1} (wavenumber) are common in infrared spectroscopy. Use their definitions and relationships to derive a simple equation to convert from one to the other. (*Hint:* the product of the two values equals a constant.)

14.4 Rotations

14.8. The silver hydride diatomic molecule, $^{197}Ag^{1}H$, has an internuclear bond distance of 1.617 Å. Predict the energies, in joules, of its first four rotational levels. (Use $I = \mu r^2$.)

14.9. Classify the following molecules as linear, spherical tops, prolate symmetric tops, oblate symmetric tops, or asymmetric tops.

(a) Dimethylacetylene, $CH_3{-}C{\equiv}C{-}CH_3$

(b) Sulfur hexafluoride, SF_6

(c) The phosphate ion, $PO_4{}^{3-}$

(d) Glycine, $CH_2(NH_2)(COOH)$

(e) *cis*-1,2-Dichloroethylene

(f) *trans*-1,2-Dichloroethylene

(g) Hexamethylbenzene, $C_6(CH_3)_6$

(h) Diacetylene, $CH{\equiv}C{-}C{\equiv}CH$

(i) The cyanide radical, CN·

14.10. Diatomic sulfur, S_2, was detected in the tail of Halley's comet when it last approached Earth in 1985–86. It has a bond length of 1.880×10^{-10} m. Calculate the value of *B*, in units of cm^{-1} and J, for S_2.

14.11. Calculate the values for *B* of SF_6 and UF_6, which are both octahedral molecules. The S–F bond distance is 1.564 Å, and the U–F bond distance is 1.996 Å. Comment on the differences between the two *B* values, keeping in mind that the atomic weight of S is 32.06 and that of U is 238.0.

14.12. The moments of inertia for phosphine, PH_3, are $5.478 \times 10^{-47}\ kg{\cdot}m^2$, $5.478 \times 10^{-47}\ kg{\cdot}m^2$, and $6.645 \times 10^{-47}\ kg{\cdot}m^2$. Calculate the rotational constants *A*, *B*, and *C* for phosphine.

14.13. Show that the degeneracy of rotational levels for symmetric tops is $2(2J + 1)$ unless $K = 0$, for which the degeneracy is $2J + 1$.

14.14. Calculate the values of the first five rotational energy levels of phosphine, PH_3. Use the values of the moments of inertia given in exercise 14.12, above.

14.15. Calculate the values of the first five rotational energy levels of ethane, CH_3CH_3, assuming it is in its energetically minimal staggered conformation. The moments of inertia for ethane are $1.075 \times 10^{-46}\ kg{\cdot}m^2$, $4.200 \times 10^{-46}\ kg{\cdot}m^2$, and $4.200 \times 10^{-46}\ kg{\cdot}m^2$.

14.5 Rotational Selection Rules

14.16. Which of the following molecules should have pure rotational spectra?

(a) Deuterium, D_2 (D is ^2H)

(b) Carbon monoxide, CO

(c) *cis* -1,2-Dichloroethylene

(d) *trans*-1,2-Dichloroethylene

(e) Chloroform, $CHCl_3$

(f) Buckminsterfullerene, C_{60}

(g) Dimethyltriacetylene, $CH_3{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CH_3$

(h) Cyanotetraacetylene, $H{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$ (Such molecules have been detected in interstellar space.)

(i) Nitric oxide, NO

(j) Nitrogen dioxide, NO_2.

14.17. The following are sets of rotational quantum numbers (J, M_J, K). Label each indicated transition as either allowed or forbidden. *Hint:* remember the rules for allowed values of the various quantum numbers.

(a) $(0, 0, 0) \rightarrow (1, 1, 0)$

(b) $(0, 0, 0) \rightarrow (-1, 0, 0)$

(c) $(3, 2, 1) \rightarrow (3, 1, 1)$

(d) $(4, 4, 1) \rightarrow (2, 4, 1)$

(e) $(5, 4, 0) \rightarrow (3, 6, 0)$

(f) $(8, 2, 2) \rightarrow (9, 2, 2)$

(g) $(7, 4, 2) \rightarrow (7, 4, 2)$

(h) $(4, 2, 5) \rightarrow (3, 2, 5)$

14.6 Rotational Spectroscopy

14.18. Having used a spectrometer to measure a simple *rotational* spectrum, you plot it in units of wavenumbers, cm^{-1}. How do you expect the spectrum to look? Convert the absorption energies to units of wavelength and replot. Are the absorptions equally spaced? Why or why not?

14.19. The rotational spectrum of $^{127}I^{35}Cl$ consists of lines equally spaced by $0.114\ cm^{-1}$. Calculate the bond distance for iodine monochloride.

14.20. Lithium hydride, $^7Li^1H$, is a potential fuel for fusion reactors because it is one of the few compounds of very small elements that exists as a solid, and is therefore more dense than gaseous fuels even under extreme conditions. LiH in the gas phase has a pure rotational spectrum consisting of lines spaced by 15.026 cm^{-1}. Calculate the bond distance in LiH.

14.21. Determine the first four absorptions in the pure rotational spectrum of LiH (see exercise 14.20) in units of GHz.

14.22. Determine the most populated rotational level, J_{max}, for a sample of LiH (see problem above) at **(a)** 298 K, **(b)** 1000 K, **(c)** 5000 K.

14.23. Given a pure rotational spectrum of the HS radical diatomic molecule ($r \approx 1.40$ Å), you notice that the most intense absorption is assigned to the $J = 8 \rightarrow J = 9$ transition. Estimate the sample temperature.

14.24. A gas-phase sample is subjected to an electric field, and its Stark-effect rotational spectrum is measured. How many individual lines will be detected for the following transitions? **(a)** $J = 0 \rightarrow J = 1$ **(b)** $J = 1 \rightarrow J = 2$ **(c)** $J = 2 \rightarrow J = 3$

14.25. From the data in Table 14.2, predict B for DCl (D is ^2H).

14.7 Centrifugal Distortions

14.26. Verify equation 14.26.

14.27. An acquaintance remarks that a rotational spectrum of I_2 showing the $J = 200 \rightarrow J = 201$ transition is predicted very closely by the rigid rotor equations from quantum mechanics. Give two reasons why you should question the validity of that statement.

14.28. Consider the values in Table 14.2 and remark on the trend of the magnitudes of B and D versus atomic mass. Does the trend make sense?

14.29. Using the value of $\tilde{\nu} = 4320$ cm^{-1} for diatomic hydrogen and the value of B for H_2 from Table 14.2, approximate D_J and compare it to the values given in Table 14.2.

14.8 & 14.9 Vibrations and Normal Modes

14.30. Determine the number of total degrees of freedom and the number of vibrational degrees of freedom for the following molecules. **(a)** Hydrogen fluoride, HF **(b)** Hydrogen telluride, H_2Te **(c)** Buckminsterfullerene, C_{60} **(d)** Phenylalanine, $C_6H_5CH_2CHNH_2COOH$ **(e)** Naphthalene, $C_{10}H_8$ **(f)** The linear isomer of the C_4 radical **(g)** The bent isomer of the C_4 radical

14.31. How many total normal modes of vibration do the molecules in the previous problem have?

14.32. Methane, CH_4, has only two IR-active vibrational modes. Comment on the expected number of IR-active vibrational modes of CH_3D, where one hydrogen atom is replaced by a deuterium.

14.10 Quantum Mechanics and Vibrations

14.33. Show that the two expressions in equation 14.30 are equivalent.

14.34. Verify that the ratio of vibrational frequencies used originally in Example 14.12 does reduce to $\tilde{\nu}^*/(2886\ cm^{-1}) = \sqrt{\mu/\mu^*}$.

14.35. Considering reduced mass can sometimes yield useful approximations even if a replaced atom isn't an isotope. Consider CO_2 and OCS. The symmetric C=O stretching vibration occurs at 1338 cm^{-1}. Estimate the frequency of the stretching vibration of the C=S bond *assuming* that the S atom is an isotope of oxygen. (It appears at 859 cm^{-1}.) Is this a good approximation or not?

14.36. The FeH diatomic molecule absorbs infrared light having a frequency of 1661.0 cm^{-1}. Assuming that this is for ^{56}FeH, calculate the frequency of light that ^{54}FeH would absorb.

14.11 Vibrational Selection Rules

14.37. Why is nitrogen gas commonly used as a purge gas in infrared spectrometers?

14.38. From the description in the text of the vibrational motions of the carbon dioxide molecule, draw arrows on each atom indicating how the atoms are moving for each normal mode. Draw a final arrow (if possible) indicating the direction of any fleeting dipole moment, and state whether each normal mode will be IR-active. (See Figure 14.30.)

14.39. Differentiate between fundamental vibrations, overtone vibrations, and hot bands. What are the selection rules for the vibrational quantum number for each?

14.40. Are deviations from an ideal harmonic oscillator more likely to be seen at low energies or high energies? Explain your answer.

14.12 Vibrations of Diatomic and Linear Molecules

14.41. Prove that $\partial^2 V/\partial r^2 = k$, the force constant. Show that the units on V (energy) and k (N/m) are consistent with this equation.

14.42. Use Figure 14.29 to comment on the variances between a Morse oscillator and a true molecular potential energy curve.

14.43. Using the information in Table 14.4, calculate D_e and the Morse potential constant a for HF ($k = 965.1$ N/m) and HBr (411.5 N/m). Express the constant a in units of m^{-1} and $Å^{-1}$. Combining your answer with the value of a for HCl in Example 14.15, do you see any trends?

14.44. Use the equation for the energy of a Morse oscillator and calculate the values for the five transitions listed for HCl in Table 14.3. How close are the predicted vibrational transitions to the experimental values in the table?

14.45. Use the ν_e values from Table 14.4 to calculate anharmonicity constants x_e and $\nu_e x_e$ for HBr and CO, and compare them to the tabulated values. Use D_0 (HBr) = 362 kJ/mol and D_0 (CO) = 1071 kJ/mol.

14.46. In exercise 14.36 above, the vibrational frequency of FeH was given as 1661 cm^{-1}. That is the *observed* vibrational frequency, not the *harmonic* vibrational frequency. Equation 14.39 can be used to determine that the observed frequency, ν, is related to the harmonic frequency ν_e and the anharmonicity $x_e\nu_e$ by the equation

$$\nu = \nu_e - 2x_e\nu_e$$

Assume that for a deuterated molecule, the frequency of the shifted vibration occurs at

$$\nu^* = \rho\nu_e - 2\rho^2 x_e\nu_e$$

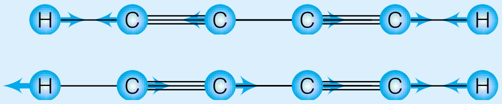
where ρ is the square root of the ratio of the reduced masses, $\sqrt{\mu/\mu^*}$. FeD absorbs light having a frequency of 1203 cm^{-1}. From this information, calculate the harmonic vibrational frequencies and the anharmonicity constants for FeH and FeD. (*Source:* A. Dendramis, R. J. Van Zee, W. Weltner, Jr. *Astrophys. J.* 1979, 231: 632–36.)

14.47. Derive the two equations used to solve exercise 14.46, using equation 14.39 and the concept of reduced mass. You will need to consider equation 14.40 as well.

14.13 & 14.14 Symmetry and Vibrations, Nonlinear Molecules

14.48. From Figure 14.32, label the normal modes of NH_3 with their proper irreducible representation.

14.49. Consider the following two vibrational modes of diacetylene, HC≡C–C≡CH:



Determine their irreducible representation labels. Which (if either) of these vibrational modes is expected to be IR-active for symmetry reasons, and why?

14.50. Each of the following pairs of molecules has the same number of atoms. In each pair, which one would you expect to have fewer *different* vibrational frequencies? You may have to determine the symmetry of each molecule before you can make a determination. **(a)** HCl and Cl_2 **(b)** H_2O $_2$ and C_2H_2 **(c)** CH_4 and XeF_4 **(d)** PF_5 and CH_3CN **(e)** $Ca_3(PO_4)_2$ and C_6H_5OH.

14.51. List the individual symmetry elements for the following point groups as either proper rotations or improper rotations. **(a)** C_{3v} **(b)** T_d **(c)** D_{6h} **(d)** S_4 **(e)** $D_{\infty h}$ **(f)** O (*not* O_h!)

14.52. Determine the number of IR-active vibrations for benzene, C_6H_6. Does it agree with the material in the text?

14.53. Determine the number of IR-active vibrations for the following molecules. You may have to determine their symmetry first. **(a)** Hydrogen peroxide, H_2O_2 **(b)** Oxalic acid, $(COOH)_2$ **(c)** Sulfur trioxide, SO_3 **(d)** Formaldehyde, H_2CO **(e)** Acetone, $(CH_3)_2CO$ (assume C_{2v} symmetry)

14.54. Determine the number of IR-active vibrations for the following molecules. You may have to determine their symmetry first. **(a)** CH_4 **(b)** CH_3Cl **(c)** CH_2Cl_2 **(d)** $CHCl_3$ **(e)** CCl_4 Do the answers make sense as you progress from methane to fully substituted methane?

14.55. How would you determine if KrF_4, if it were synthesized, had tetrahedral or square planar geometry?

14.56. Determine the number of IR-active vibrations for the following molecules. You may have to determine their symmetry first. **(a)** F_2O **(b)** NCl_3 **(c)** $N(CH_3)_3$ (assume C_{3v} symmetry)

14.57. Verify that cubane, C_8H_8, has only three IR-active vibrations and determine the degeneracies of each. How many total vibrations out of the 42 vibrational degrees of freedom are thus represented by the three IR-active vibrational motions?

14.15 & 14.16 Nonallowed, Nonfundamental Vibrations and Fingerprint Regions

14.58. Carbon dioxide has the following fundamental vibrational frequencies:

$$\nu_1 = 667\ \text{cm}^{-1} \qquad \nu_2 = 1338\ \text{cm}^{-1} \qquad \nu_3 = 2349\ \text{cm}^{-1}$$

According to the literature (K. E. Dierenfeldt, *J. Chem. Ed.,* 1995, 72: 281–83), the following combination bands appear in the spectrum: 618, 2337, and 3715 cm^{-1}. Assign these to the proper combinations of the fundamental vibrations.

14.59. Would you expect the above combination absorptions to be strong or weak in a spectrum? Why?

14.60. Why is it possible to identify fingerprint regions for overtone transitions and hot bands but not for combination bands?

14.61. Dioctyl sulfide, $(C_8H_{17})_2S$, and hexadecane, $C_{16}H_{34}$, have very similar vibrational spectra. Use a correlation table to explain why.

14.62. Where would you expect vibrations for ethyl alcohol, CH_3CH_2OH, to appear in a vibrational spectrum?

14.17 Rovibrational Spectroscopy

14.63. Silane, SiH_4, has a tetrahedral geometry and a rovibrational spectrum consisting of lines spaced by 16.72 cm^{-1}. Calculate the Si–H bond distance in silane. Could this information be obtained by pure rotational spectroscopy? Why or why not?

14.64. Electronic energy level transitions typically have higher energies than vibrational energy levels. Would the equivalent of *P*, *Q*, or *R* branches appear in electronic spectra if Δv were -1, 0, or 1? Justify your answer.

14.65. What are the forms of equations 14.41 and 14.42 if centrifugal distortion is negligible?

14.66. The table in exercise 14.71 lists some frequencies of absorptions in a *P* branch and an *R* branch. Why is there no line listed as *P*(0)?

14.18 Raman Spectroscopy

14.67. Two Raman spectra are measured on the same sample. One spectrum uses the red He-Ne laser light, at 632.8 nm, as a source; the other uses the 568.2-nm light from a Kr^+ laser. How are the two spectra different? How are the two spectra the same?

14.68. Determine the number of Raman-active vibrations for the following molecules. You may have to determine their symmetry first.

(a) CH_4 **(b)** CH_3Cl **(c)** CH_2Cl_2 **(d)** $CHCl_3$ **(e)** CCl_4

Compare your results with the answers to exercise 14.54, above.

14.69. The *mutual exclusion rule* states that for certain molecules, vibrations that are IR-active are not Raman-active, and vice versa. Molecules must have a certain symmetry element in order for the mutual exclusion rule to apply. Examine the character tables in Appendix 3 and determine what that symmetry element is.

14.70. Is xenon tetrafluoride, XeF_4, tetrahedral or square planar? IR and Raman spectra each show three vibrations. Use the GOT and analyses like those in Examples 14.19 and 14.22 to propose a structure for this molecule.

Symbolic Math Exercises

14.71. Several equations can be derived from equations 14.41 and 14.42 and used to determine, graphically or numerically, the various molecular parameters for a molecule from rovibrational spectral data: Two of them are

$$\frac{R(J) - P(J)}{4(J + \frac{1}{2})} = B_1 - 2D_J(J^2 + J + 1)$$

$$\frac{R(J-1) - P(J+1)}{4(J + \frac{1}{2})} = B_0 - 2D_J(J^2 + J + 1)$$

where $R(J)$ is the line in the R branch that originates from the J rotational level and $P(J)$ is the line in the P branch that originates from the J rotational level. Use the following data to determine B_0, B_1, and D_J for HCl. All numbers are in units of cm^{-1}.

		$R(0)$	2906.047
$P(1)$	2864.825	$R(1)$	2925.814
$P(2)$	2843.370	$R(2)$	2944.859
$P(3)$	2821.433	$R(3)$	2963.180
$P(4)$	2798.773	$R(4)$	2980.777
$P(5)$	2775.631	$R(5)$	2997.893
$P(6)$	2751.765	$R(6)$	3014.286
$P(7)$	2727.658	$R(7)$	3029.955

14.72. Use equation 14.17 to determine the energies of rotation for ammonia, NH_3, as the rotational quantum number J ranges from 1 to 10. ($I_a = I_b = 4.413 \times 10^{-47}\ \text{kg·m}^2$, $I_c = 2.806 \times 10^{-47}\ \text{kg·m}^2$) Then, construct an energy level diagram for all of the rotational levels, and label them with J and K quantum numbers. What are the degeneracies of the levels?

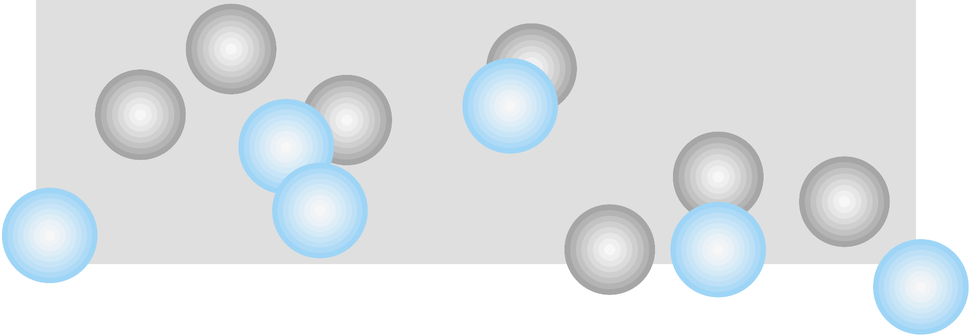
14.73. What are the energy changes for the allowed rotational transitions from the energy level diagram constructed in exercise 14.72?

14.74. Construct and compare the energy level diagrams for the rotations of a diatomic molecule assuming it acts as a rigid rotor (equation 14.21) and a rigid rotor with centrifugal distortion corrections (equation 14.26). Use HBr as a model system, where $B = 8.473\ \text{cm}^{-1}$ and $D_J = 3.72 \times 10^{-4}\ \text{cm}^{-1}$. Compare rotational levels up to $J = 20$.

14.75. Construct and compare energy level diagrams for vibrations of an ideal harmonic oscillator and an anharmonic oscillator. Use HCl as a model oscillator, and compare levels up to $v = 25$. Use $\nu_e = 2989.74\ \text{cm}^{-1}$ and $\nu_e x_e = 52.05\ \text{cm}^{-1}$.

15

Introduction to Electronic Spectroscopy and Structure



DESPITE THE FACT THAT WE TREATED vibrational and rotational spectroscopy first, the astute student will recognize that one of the mysteries of classical mechanics involved electronic spectroscopy. The inability to explain the (electronic) spectrum of the hydrogen atom was a major reason for the development of quantum mechanics. Yet, we have put off a detailed discussion of it until after considering rotational and vibrational spectra.

The reason for the delay is that a detailed discussion is slightly more complicated for electronic spectra than for rotations or vibrations. Some new ideas will have to be developed in order to begin to understand the electronic spectra and structures of many-electron systems. (We should recognize that the electronic spectrum of hydrogen, even in the formalism of quantum mechanics, will be relatively simple.) However, as with rotational and vibrational spectroscopy, our treatment of electronic spectroscopy in this chapter is limited by necessity. Entire books are written on the subject, and we can only introduce some basic ideas here.

15.1 Synopsis

We will start by considering the selection rules for electronic transitions. Then, we will consider the electronic spectrum of the hydrogen atom in terms of the selection rules and quantum mechanics. There will be few if any surprises here, since the positions of the lines of the hydrogen atom's spectrum were at least known (but not completely understood) over a hundred years ago. The electronic spectrum of helium, the simplest multielectron system, is not so easy to model mathematically. This is expected, since quantum mechanics cannot determine analytic expressions for the wavefunctions for the helium atom. An electronic spectrum, which shows *changes* in energies, is equally nonanalytic. However, for helium and larger atoms (and molecules), we will find that certain regularities in the spectrum can be traced back to the angular momentum of the electrons in the atom or molecule. Ultimately, the angular momentum—which was central to Bohr's theory of hydrogen—will have a central role in our understanding of electronic spectra. We will see how it is utilized in atomic, diatomic, and (briefly) molecular electronic spectra.

Some molecules have electronic structures that are more easily described than others. The π electron system of aromatic molecules is an example, and we will discuss it briefly—but in enough detail to understand exactly where the important idea of aromaticity comes from. Fluorescence and phosphorescence are two electronic phenomena that show how complex the interactions of electronic wavefunctions can get. Finally, we will introduce lasers. Although laser action can be due to transitions among vibrational, rotational, chemical, or even translational energy levels, the original lasers were dependent on electronic transitions. Given the prevalence of lasers in modern society, it is perhaps only fitting that we end the chapter with an introduction to these powerful light sources.

15.2 Selection Rules

As with rotational and vibrational transitions, there is a selection rule for electronic transitions dictating which electronic wavefunctions participate in allowed transitions. Allowed electronic transitions must have a nonzero transition moment as given by the expression

$$M = \int \Psi^*_{\text{final}} \hat{\mu} \Psi_{\text{initial}} \, d\tau \tag{15.1}$$

where now Ψ_{initial} and Ψ_{final} refer to wavefunctions of the system of interest. $\hat{\mu}$ is the electric dipole operator that defines the interaction between light and matter. In rotational and vibrational spectroscopy, the selection rules we could derive from equation 15.1 were relatively straightforward in terms of changes in rotational and vibrational quantum numbers.

Unfortunately, for electronic transitions, gross selection rules are not as straightforward to define. Therefore, we will consider the selection rules for electronic transitions as they arise in the discussion of the material. The electronic spectrum of the hydrogen atom, for example, has a relatively simple selection rule. The electronic spectrum of the benzene molecule, as a counterexample, follows more complex rules.

There is one assurance with regard to electronic spectra. Recall that allowed transitions for both rotational and vibrational spectra depend on the presence of a dipole moment, either a permanent one or a changing one. Allowed electronic transitions always occur with a change in the electronic charge distribution in an atom or molecule. (This change is sometimes referred to as a “dipolar shift.”) This statement is easily justified. An electron whose state is described by an initial wavefunction has probabilities of existing in certain locations in an atomic or molecular system. When described by a *different* wavefunction, the electron has different probabilities of existing in those locations. The electron probability distribution has *changed.* Allowed electronic transitions are therefore intimately tied to the idea of a changing electronic charge, just like allowed rotational and vibrational transitions.

Specific selection rules for atoms and molecules can also be determined using group-theoretical analyses of the functions in equation 15.1, exactly as we did in the previous chapter for allowed IR and Raman vibrational transitions.

15.3 The Hydrogen Atom

Recall that when an electric current is passed through a sample of hydrogen gas, light is given off and this light has certain specific frequencies. The interpretation that this light is emitted by electronic transitions was firmly established by Bohr, who derived the equation

$$\frac{1}{\lambda} = R\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{15.2}$$

by assuming that the angular momentum of the electron is quantized. λ is the wavelength of the light, R is called the Rydberg constant, and n_1 and n_2 are *quantum numbers*. Quantum mechanics provides a similar equation for the spectrum of the hydrogen atom (albeit from different assumptions, namely that the wavefunctions of electrons in hydrogen must satisfy the Schrödinger equation). Quantum mechanics also determines that the Rydberg constant R is

$$R = \frac{e^4\mu}{8\epsilon_0^2 h^2} \tag{15.3}$$

where the constants in the above expression have their usual meaning. The relative simplicity of the spectrum of the hydrogen atom is based on equation 15.2, which is itself based on experiment (that is, observation). And so a "selection rule" of sorts can be stated for electronic transitions in the hydrogen atom: allowed transitions are dictated by changes in the principal quantum number.

However, this is misleading. Although electronic energy levels are dictated by the principal quantum number, we should remember that a principal quantum shell in a hydrogen atom has other quantum numbers, namely ℓ and m_ℓ. If the symmetries of the operator and wavefunctions in equation 15.1 were examined, one would find that it is the *angular momentum quantum number* ℓ that dictates the selection rule. The specific selection rule for allowed electronic transitions in the hydrogen atom (or, for that matter, hydrogen-like atoms) is

$$\Delta\ell = \pm 1 \tag{15.4}$$

Since photons themselves have an angular momentum, this selection rule is consistent with the law of conservation of angular momentum. There is also a potential effect on the m_ℓ quantum number, since the change in the ℓ quantum number may or may not occur in the z component of the total angular momentum. Therefore, the accompanying selection rule is

$$\Delta m_\ell = 0, \pm 1 \tag{15.5}$$

There is no restriction on the change in n, the principal quantum number. Δn can have any value. Why are the selection rules, equations 15.4 and 15.5, not obvious from the spectrum of the hydrogen atom? Because the electronic energy of the hydrogen atom does not depend on the angular momentum quantum number. It depends only on the *principal* quantum number, n. The spatial wavefunctions of the hydrogen atom are n^2-fold degenerate because of variations in the ℓ and m_ℓ quantum numbers, so the spectrum of the hydrogen atom *appears* as if the energy differences are due to changes in the principal quantum number.* In reality, the spectral lines are due to electrons changing not just their principal quantum number but also, according to the selection rule, their angular momentum quantum number.

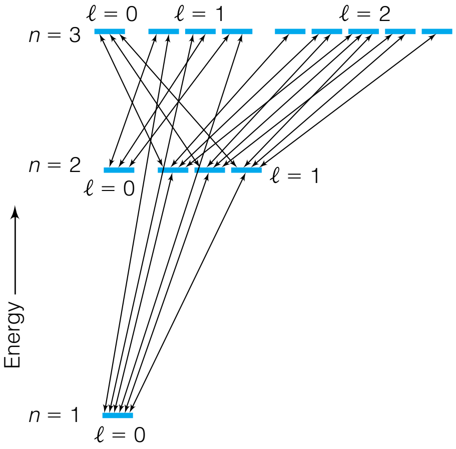


Figure 15.1 Some of the allowed transitions of the single electron in the hydrogen atom. Despite the complexity of the diagram, the hydrogen atom's electronic spectrum is relatively simple because the subshells within the same principal quantum number are degenerate.

Figure 15.1 shows some of the transitions that are possible according to the selection rule above. For several of the possible changes in the n quantum number, the $\Delta\ell$ changes are different but lead to the same ΔE (which is what

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*They are $2n^2$-fold degenerate if the spin of the electron is included.

a spectrum illustrates). Since the energy of the transition depends on the value of n and not of ℓ, the different transitions ultimately have the same ΔE.

Example 15.1

Which pairs of transitions [indicated by the (n, ℓ, m_ℓ) quantum numbers] of the hydrogen atom occur with the same value of ΔE?

a. $(2, 1, 1) \rightarrow (3, 2, 2)$ and $(3, 2, 2) \rightarrow (4, 1, 2)$

b. $(3, 1, 0) \rightarrow (5, 2, 1)$ and $(3, 4, 0) \rightarrow (5, 3, 0)$

Solution

a. Since the two transitions are occurring between different values of the principal quantum number, these two transitions do not have the same ΔE value and would be seen at different wavelengths in the spectrum.

b. Even though the ℓ and m_ℓ quantum numbers are different, because the transitions occur between wavefunctions having the same principal quantum number, the energies of transition are the same.

The above example and selection rules are also applicable to hydrogen-like ions, which have a single electron. However, such systems are in the vast minority of atomic species whose spectra need to be understood. Recall that one of the final failings of classical mechanics was the inability to explain spectra. Although quantum mechanics does not provide analytic solutions for wavefunctions of multielectron systems, it does provide tools for understanding it.

15.4 Angular Momenta: Orbital and Spin

In the discussion of the 2-D and 3-D rigid rotors, the concept of angular momentum arose, and in particular we used the fact that the angular momentum of an object in some circular motion is related to its energy. For three dimensions, the wavefunctions are the spherical harmonics, and the eigenvalue energies E are dependent on an angular momentum quantum number ℓ such that

$$E = \frac{\ell(\ell + 1)\hbar^2}{2I}$$

where ℓ is the angular momentum quantum number, $\hbar$ is Planck's constant divided by 2π, and I is the moment of inertia. In the case of a 3-D rigid rotor, the angular momentum is a well-understood classical property. In the application of the 3-D rigid rotor to the hydrogen atom, the total electronic energy is determined by the principal quantum number n, but the electron in the hydrogen atom has definite angular momentum values due to its *orbital* angular momentum.

An electron in a hydrogen atom also has spin. Spin acts like an angular momentum, so it is proper to speak not only of orbital angular momentum but also of *spin* angular momentum. The two different types of angular momenta of an electron will each generate an intrinsic magnetic field, as will any charged species that has angular momentum (that is, that accelerates by moving in some sort of circular motion). These two intrinsic magnetic fields will interact with each other in such a way that they combine to make an *overall* angular momentum. It is this overall angular momentum, the combination of orbital angular momentum and spin angular momentum, that determines the total electronic eigenvalue energy and thus dictates the changes in energy recorded in an electronic spectrum. It is important, then, to understand how the orbital and spin angular momenta interact. This interaction is called *spin-orbit coupling.* Spin-orbit coupling acts to make individual electronic energies slightly different from the equation above, depending on how the spin angular momentum is interacting with the orbital angular momentum. The overall effect is to *split* the energy levels into a larger number of discrete energy levels. The net result is that the electronic spectrum of a multielectron atom is more complicated.

Experiments have indicated that the total angular momentum and the z component of the total angular momentum for an electron are quantized. (This situation is very similar to the rotations of molecules.) As such, the allowed values for total angular momenta quantum numbers are similar to those for orbital or spin angular momenta. We will adopt the convention of using the quantum numbers ℓ and m_ℓ to refer to the orbital angular momenta of an electron, s and m_s to label the spin angular momenta, and introduce the quantum numbers j and m_j to refer to the total angular momentum and the z component of the total angular momentum for a single electron. As with all angular momenta, m_j can have $2j + 1$ possible values, ranging from $-j$ to j. We also adopt the convention of using capital letters for the various quantum numbers for the total angular momenta of several electrons. We will use ℓ, m_ℓ, and so on for a single electron, but L, M_L, S, M_S, J, and M_J for the various combined momenta of more than one electron.

Orbital and spin angular momenta combine (that is, couple) in vector fashion. Consider the electron having $\ell = 0$ (that is, an electron in the s subshell) as shown in Figure 15.2. The spin angular momentum s is always $\frac{1}{2}$ for an electron, but it can be oriented in two different directions (corresponding to the quantum number m_s having values of $+\frac{1}{2}$ or $-\frac{1}{2}$). The total angular momentum, labeled by the quantum number j, is determined from the combination of the ℓ and s values, or simply $\frac{1}{2}$. However, the j vector can have two possible orientations with respect to the z-axis, corresponding to two different possible values of m_j, as shown in Figure 15.2.

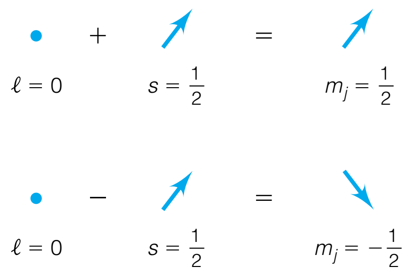

Figure 15.2 The combination of the orbital angular momentum of an s-subshell electron (represented by a single dot) with the spin angular momentum yields a total angular momentum j of $\frac{1}{2}$ that can have two possible z orientations, corresponding to $m_j = \frac{1}{2}$ *and* $m_j = -\frac{1}{2}$, as shown.

For a single p-subshell electron, j can have two possible values, corresponding to the two possible vector combinations of the ℓ vector (which has magnitude 1) and the s vector (which has magnitude $\frac{1}{2}$). This is illustrated in Figure 15.3. For the p electron:

$$j = \ell + s \quad \text{or} \quad \ell - s \tag{15.6}$$

$$= 1 + \frac{1}{2} \quad \text{or} \quad 1 - \frac{1}{2}$$

$$j = \frac{3}{2} \quad \text{or} \quad \frac{1}{2}$$

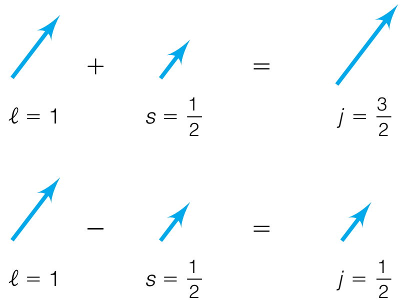

Figure 15.3 The combination of the orbital angular momentum of a p-subshell electron (represented by a vector) with the spin angular momentum can also lead to two possible total angular momenta. Compare with Figure 15.2.

Generally, the possible values of j are

$$j = \ell + s \longrightarrow |\ell - s| \quad \text{in integer steps} \tag{15.7}$$

where the arrow means "through." For $j = \frac{1}{2}$, m_j can be either $-\frac{1}{2}$ or $\frac{1}{2}$, just as for the single s electron. However, for $j = \frac{3}{2}$, m_j can have values of $-\frac{3}{2}$, $-\frac{1}{2}$, $\frac{1}{2}$, or $\frac{3}{2}$. Thus, the single p electron has more possible values for its total angular momentum, and more possible z components of its total angular momentum, than a single s electron.

Example 15.2

From the above expressions, determine the possible values of j for the following.

a. A single d electron

b. A single h electron (where $\ell = 5$)

Solution

a. For a d electron, $\ell = 2$ and s always equals $\frac{1}{2}$, so the two possible values of j for a single d electron are $\frac{5}{2}$ and $\frac{3}{2}$.

b. For an h electron (which would exist as an excited state in, say, the sixth principal quantum shell), $\ell = 5$, so the two possible values of j for a single h electron are $\frac{11}{2}$ and $\frac{9}{2}$.

This example again shows the possible values for the j quantum number as half-integers. For single electrons j is always a half-integer. For multiple electrons, J can be either integers or half-integers.

Example 15.3

What are the possible values of m_j for the d electron in Example 15.2?

Solution

For an angular momentum that follows the normal quantum-mechanical rules for angular momenta, the possible values of m_j range from $-j$ to j, in integer steps. Therefore, $m_j = -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$, and $\frac{5}{2}$ for the $j = \frac{5}{2}$ state, and $-\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}$, and $\frac{3}{2}$ for the $j = \frac{3}{2}$ state of the d electron. There are six possible values of m_j for $j = \frac{5}{2}$ and four possible values of m_j for $j = \frac{3}{2}$.

The point of this example is worth repeating: for an electron that has a total angular momentum indicated by the quantum number j, the possible values of m_j are

$$m_j = -j \text{ to } j \text{ in integer steps} \quad (2j + 1 \text{ possible values}) \tag{15.8}$$

The *overall* energy of an electron is dependent on the value of the j quantum number. The m_j quantum number does not affect the energy of the electron unless the atom is in the presence of a magnetic or electric field. These statements are consistent with the known effects of ℓ and m_ℓ on the energy of a (hydrogen-like) electron.

Completely filled subshells (not shells, but subshells) contribute no overall angular momentum to the total angular momentum of the atom. All angular momenta, orbital and spin, are paired so that there is a net zero effect. However, if an electron from a filled subshell is excited to a higher-energy state, this statement no longer applies and the effect on the total angular momentum by the partially filled subshell as well as the excited electron must be taken into account.

However, first we ought to be able to obtain some understanding of the electronic spectra of atoms that have a single electron in their valence subshell. Such atoms have the electron configurations ns^1, np^1, nd^1, or nf^1 (where n is some allowed value of the principal quantum number). Because of the lone valence electron in such atoms, selection rules are dictated by the allowed changes in ℓ and m_ℓ:

$$\Delta\ell = \pm 1$$

$$\Delta m_\ell = 0, \pm 1$$

The values of the j quantum number depend on the values of the ℓ and m_ℓ quantum numbers. In these cases, no selection rule depends on j (although it is recognized that the value of the j quantum number is dictated by the respective values of ℓ and m_ℓ).

Example 15.4

In his pioneering investigations around 1814 into the spectrum of the sun, Joseph von Fraunhofer labeled an intense yellow line of the spectrum with the letter D. It was shown that this emission was due to the sodium atom (indicating, by the way, the presence of sodium in the sun), so this was eventually termed the "sodium D line." Later work showed that under high resolution the sodium D line is actually a pair of closely spaced lines, separated by 6 Å. Assuming that in the lower electronic state of the sodium atom the valence electron has the quantum numbers $(n, \ell, j) = (3, 0, \frac{1}{2})$, what are the possible quantum numbers for the upper electronic state?

Solution

Since there is no selection rule for Δn, we cannot say which principal quantum number can be assigned to the upper electronic state. (It is actually due to an $n = 3$ to $n = 4$ transition.) However, we can use the selection rules for ℓ and m_ℓ to determine what the quantum numbers for the upper electronic state must be for intense—and presumably allowed—transitions. Since $\ell = 0$ for the lower state, the upper state must have $\ell = 1$ (since $\ell = -1$ is not possible). This means that the upper electronic state must be a p orbital. Since the m_ℓ quantum number for the lower electronic state must be 0 ($\ell = 0$ means that m_ℓ must be 0), then the upper electronic state must have an m_ℓ of either -1, 0, or 1. Such states are degenerate unless a magnetic field is present. However, for a single electron, $s = \frac{1}{2}$, so from the upper state's value of ℓ we can determine that the possible j values are $\frac{1}{2}$ or $\frac{3}{2}$. There are, then, two possible combinations of quantum numbers for the upper state: $(n, \ell, j) = (n, 1, \frac{1}{2})$ or $(n, \ell, j) = (n, 1, \frac{3}{2})$. The different quantum numbers—j, in particular—imply that there will be a slightly different energy for the two upper states. This is the reason there are two closely spaced lines in the spectrum of Na.

Although this is a relatively simple example, it points out a key factor in the understanding of electronic spectra of atoms: the fact that orbital and spin angular momenta interact, or *couple*. Coupling is even more important in the understanding of electronic spectra of atoms that have more than one electron in their valence subshell, because now the orbital and spin angular momenta of different electrons can couple *with each other*. This makes the spectra potentially more confusing. Luckily, there is a procedure for formalizing the coupling possibilities between more than one electron in a valence subshell. That will be considered in the next section.

15.5 Multiple Electrons: Term Symbols and Russell-Saunders Coupling

Understanding the momentum combinations of lone electrons in a subshell is straightforward. But what about the majority of atomic systems, neutral or ionized, that have more than one electron in the outermost subshell? How do we understand all the possible ways the orbital and spin angular momenta of multiple electrons can interact?

Two common systems are used to understand multiple-electron spin-orbit coupling. They are called the *Russell-Saunders coupling scheme* and the *j-j coupling scheme*. The Russell-Saunders (or RS) coupling scheme is valid for low-Z (that is, low atomic number, typically 30 or lower) atoms where spin-orbit coupling is relatively weak. It treats total orbital angular momentum of multiple electrons separately from the total spin angular momentum. The *j-j* coupling scheme is used for high-Z ($Z > 30$) atoms in which spin-orbit coupling is so large that a total angular momentum j for each individual electron must be determined first. We will consider the RS coupling scheme exclusively in this text.

Before we consider the coupling scheme, we need to introduce the idea of the term symbol. We will be working with total orbital angular momenta and total spin angular momenta, and being vector quantities the individual angular momenta of two or more electrons can combine. A *term symbol* is a shorthand device for indicating the values of the orbital, spin, and total angular momenta of an electronic state (and since the energy of the state depends on the values of these angular momenta, the term symbol becomes a useful way to label an electronic state).

If L is the quantum number indicating the vector sum of the orbital angular momentum of an electronic state, and S represents the vector sum of the spin angular momentum of the electronic state, and J represents the total angular momentum of the electronic state, then the term symbol would be constructed as

$$^{2S+1}L_J \tag{15.9}$$

Instead of using the numerical value for L, a letter label is used (just like the *s*, *p*, *d*, *f*, . . . subshell designations stand for $\ell = 0, 1, 2, 3, \ldots$ in atoms). The following capital letters are used to indicate the value for L:

L	Letter designation
0	S
1	P
2	D
3	F
.	.
.	.
.	.

Such letters are commonly used to refer to various electronic states; that is, one hears of S states, P states, and so on. The left superscript is not S but $2S + 1$ (for reasons that become clear shortly). The quantity $2S + 1$ is called the *multiplicity* of the state. States that have a multiplicity of 1 are called singlet states, and states that have multiplicities of 2 are doublet states. There are also triplet, quartet, and so on, states. The right subscript, J, indicates the total angular momentum and is determined by L and S, as before. The following example shows how term symbols are constructed.

Example 15.5

What are the term symbols for the two higher-energy states in the Na atom's D lines? Use the solution to Example 15.4 for the values of the various angular momenta.

Solution

In this case, the momenta of the single valence electron dictate the total angular momenta; that is, $(L, S, J) = (\ell, s, j)$. For the two upper electronic states, the (L, S, J) quantum numbers are $(1, \frac{1}{2}, \frac{1}{2})$ and $(1, \frac{1}{2}, \frac{3}{2})$. (How did we know that $S = \frac{1}{2}$? Because for a single electron, the vector sum of the single spin angular momentum is $\frac{1}{2}$.) Since $L = 1$, both term symbols are P states, and since $S = \frac{1}{2}$ for both states, the multiplicities are both $2(\frac{1}{2}) + 1 = 2$. Therefore, the two term symbols are

$$^2\mathrm{P}_{1/2} \quad \text{and} \quad ^2\mathrm{P}_{3/2}$$

These two term symbols, and others like them, are used to label not only electronic states but also electronic transitions. For example, upon knowing that the lowest-energy ground state of the Na atom has a $^2\mathrm{S}_{1/2}$ term symbol (a fact that can be determined from the electron configuration of its valence shell), the two transitions involved in the sodium D emission lines are labeled

$$^2\mathrm{P}_{1/2} \longrightarrow {}^2\mathrm{S}_{1/2} \qquad ^2\mathrm{P}_{3/2} \longrightarrow {}^2\mathrm{S}_{1/2}$$

Such labels make it easier to express the identities of the electronic states involved in an electronic transition.

We are beginning to focus on quantum numbers L and S instead of ℓ and s (the spin for a single electron). This is because for multielectron atoms, the quantum numbers ℓ and s are not "good" quantum numbers. The quantum numbers ℓ and s were originally defined in terms of a single electron. Recall that the concepts of electron shells and subshells were defined using the hydrogen atom and then applied as an approximation to larger atoms ("electron configurations"). For multielectron systems, the eigenvalue equations involving ℓ and s are not strictly satisfied. Even though we presume to label electrons as having a principal, orbital angular momentum (total and z-component) and a spin angular momentum (again, total and z-component) using the aufbau principle, such a labeling is an approximation. A better description of reality is that an unfilled shell has a *total* orbital angular momentum L and a *total* spin angular momentum S. L and S, and subsequently J, are the good quantum numbers.

The situation is not as complicated as it might seem, because L and S are determined from the vector combinations of the individual ℓ and s quantum numbers from the electrons in the unfilled shell. Consider the simplest case, two electrons in the outermost, unfilled subshell. (Remember that filled subshells contribute no *net* orbital or spin angular momentum.) Two electrons having individual orbital angular momenta ℓ_1 and ℓ_2 can couple so that the net orbital angular momentum can have the *possible* values

$$L = \ell_1 + \ell_2 \longrightarrow |\ell_1 - \ell_2| \quad \text{in integral steps} \tag{15.10}$$

where again the arrow means "through." That is, the possible values of L range from the integers $\ell_1 + \ell_2$ through $|\ell_1 - \ell_2|$ in integral increments. The absolute values imply that L can never be negative. For example, for two

p electrons ($\ell_1 = \ell_2 = 1$), the possible values for L are 2, 1, and 0. These possible values of L indicate the possible vector combinations of the m_ℓ quantum numbers of the two electrons.

For the S of a multielectron, unfilled-subshell atom, a similar relationship applies. For the simple case of two electrons, the *possible* values of S are given by

$$S = s_1 + s_2 \longrightarrow |s_1 - s_2| \quad \text{in integral steps} \tag{15.11}$$

For electrons, $s = \frac{1}{2}$, so for two electrons the possible values of S are 1 and 0. These possible values of S correspond to the possible vector combinations of the m_s quantum numbers of the two electrons. The vector combinations of multiple ℓ and s values are similar to those depicted in Figures 15.2 and 15.3.

How do these rules help us in understanding electronic energy levels of atoms? The first step is to recognize that an atom can have all combinations of orbital and spin angular momentum—that is, all possible combinations of L and S—that are possible. The one immediate additional factor to consider is the Pauli principle. For example, the carbon atom has a ground-state electron configuration $1s^2\ 2s^2\ 2p^2$. *Within this electron configuration*, the atom can have several possible combinations of L and S, only one of which is the lowest-energy ground state. This means that there are *excited states* of the carbon atom that still have the electron configuration $1s^2\ 2s^2\ 2p^2$. Each of these states, ground and excited, will have its own term symbol, so within this electron configuration several possible term symbols label the individual energy levels. For a carbon atom, the possible values of L are 2, 1, and 0 (satisfy yourself that this is the case), and the possible values for S are 1 and 0 (again, satisfy yourself that this is true). All possible combinations of L and S lead to the following possible term symbols, J not included:

$$^1\text{S},\ ^1\text{P},\ ^1\text{D},\ ^3\text{S},\ ^3\text{P}, \text{ and } ^3\text{D}$$

Although these are all of the combinations, some of them are ruled out by the Pauli principle. For example, the term symbol ^{3}D implies that for both electrons, $m_\ell = +1$ and that the spins are oriented in the same direction (that is, the m_s for both electrons is the same). This implies that both electrons have the same set of four quantum numbers, which is forbidden by the Pauli principle. Therefore, the ^{3}D term symbol *cannot and does not exist* for this electron configuration. A similar argument can be made for the ^{3}S term: both electrons could have $m_\ell = 0$ and m_s the same, but this is forbidden by the Pauli principle. Therefore, the ^{3}S term symbol does not exist either.

The ^{1}P term symbol also does not exist, not because of Pauli principle reasons, but because the remaining term symbols collectively define all the possible ways the two p electrons can couple their orbital and spin angular momentum. A ^{1}P term symbol is redundant and therefore unnecessary. So, the possible term symbols for the ground-state *electron configuration* are

$$^1\text{S},\ ^1\text{D}, \text{ and } ^3\text{P}$$

Again, note the distinction between electron configuration and term symbols. All three of the above term symbols describe certain states of the two p electrons in the ground-state electron configuration of the carbon atom (or, for that matter, any atom that has a p^2 valence subshell). However, because they represent different total orbital and spin angular momenta, they represent states that have different total energies, even though they are for a carbon atom having a $1s^2\ 2s^2\ 2p^2$ electron configuration.

Example 15.6

List all of the possible term symbols (do not neglect any due to Pauli principle considerations) for a d^2 ground-state valence electron configuration.

Solution

Each d electron has an ℓ of 2, so the possible values of L are 4, 3, 2, 1, and 0. This implies the possible existence of G, F, D, P, and S states. Like the above example, the two electrons each have an s of $\frac{1}{2}$, so the possible values of S are 1 and 0. The resulting values of the multiplicity are 3 and 1. Combining the multiplicities with the L values, the possible term symbols are ^{3}G, ^{1}G, ^{3}F, ^{1}F, ^{3}D, ^{1}D, ^{3}P, ^{1}P, and ^{3}S, ^{1}S. (The Pauli principle and redundancy will ultimately eliminate the ^{3}S, ^{3}D, ^{3}G, ^{1}P, and ^{1}F term symbols for these atoms, leaving ^{1}G, ^{3}F, ^{1}D, ^{3}P, and ^{1}S.)

The rules for determining term symbols above (and more importantly, for excluding certain term symbols) assume that the electrons in the unfilled subshell are in the same atomic subshell. This is why we can apply the Pauli principle to exclude certain term symbols. If the electrons are in *different* subshells (as in an excited state), then we could not use the Pauli principle in this way, and more term symbols would be necessary to describe the possible interactions of the angular momenta.

All atoms having an electron configuration with a p^2 valence subshell have the same possible term symbols. A similar statement is possible for any electron configuration of a valence subshell: atoms having the same configuration have the same term symbols. Furthermore, it can be shown that atoms having an electron configuration p^4 have the same term symbols as those having a p^2 configuration. Atoms having a d^2 configuration have the same term symbols as a d^8 atom, and so on. In general, if a subshell can hold a maximum of m electrons, then the configuration of $m - n$ electrons has the same term symbols as the configuration of n electrons. (For example, d^2 and d^8 configurations have the same term symbols, d^3 and d^7 do also, and so on.) What this all implies is that there are only a limited number of possible term symbols for electron configurations. Table 15.1 lists those term symbols for electron configurations of various valence subshells. Remember that closed shells do not contribute any net angular momentum (orbital or spin), so the only subshell that must be considered is any unfilled subshell.

Table 15.1 Term symbols for partially filled subshells

Subshell	Term symbols
s^1	^{2}S
p^1, p^5	^{2}P
p^2, p^4	^{1}S, ^{1}D, ^{3}P
p^3	^{2}P, ^{2}D, ^{4}S
d^1, d^9	^{2}D
d^2, d^8	^{1}S, ^{1}D, ^{1}G, ^{3}P, ^{3}F
d^3, d^7	^{2}P, ^{2}D, ^{2}D, ^{2}F, ^{2}G, ^{2}H, ^{4}P, ^{4}F
d^4, d^6	^{1}S, ^{1}S, ^{1}D, ^{1}D, ^{1}F, ^{1}G, ^{1}G, ^{1}I, ^{3}P, ^{3}P, ^{3}D, ^{3}F, ^{3}F, ^{3}G, ^{3}H, ^{5}D
d^5	^{2}S, ^{2}P, ^{2}D, ^{2}D, ^{2}D, ^{2}F, ^{2}F, ^{2}G, ^{2}G, ^{2}H, ^{2}I, ^{4}P, ^{4}D, ^{4}F, ^{4}G, ^{6}S

Note: Atoms having completely filled subshells all have a single ^{1}S term.

So far, we have not considered the J quantum number in the term symbol, even though we defined the term symbol as listing a value for J. For each ^{2S+1}L term, the possible values of J are

$$J = L + S \longrightarrow |L - S| \quad \text{in integral steps} \tag{15.12}$$

J is also limited to positive numbers, and it depends on the values of L and S. Equation 15.12 implies that for each combination of L and S, there are several possible total angular momenta (as might be expected from the coupling of quantized angular momentum vectors). Because J is determined from L and S, tables of term symbols like Table 15.1 typically leave off the J for quantum number total angular momentum for reasons of clarity.

Now the complete term symbols can be written. For the carbon atom's p^2 configuration that has ^{1}S, ^{1}D, and ^{3}P states:

$$\begin{aligned} &^1\text{S:}\quad J = 0 + 0 \longrightarrow |0 - 0| = 0 && \text{Term symbols: } ^1\text{S}_0 \\ &^1\text{D:}\quad J = 2 + 0 \longrightarrow |2 - 0| = 2 && \text{Term symbols: } ^1\text{D}_2 \\ &^3\text{P:}\quad J = 1 + 1 \longrightarrow |1 - 1| = 2, 1, 0 && \text{Term symbols: } ^3\text{P}_2, {}^3\text{P}_1, \text{and } ^3\text{P}_0 \end{aligned}$$

Notice that of the original three states, the two that are singlets (that is, their multiplicity equals 1) have only a single complete state, and the triplet state is composed of three individual, complete term symbols. Also, recall that there is a z component of the total angular momentum J, and it has the same possible values as any z component of an angular momentum, given in equation 15.8. As such, there are $2J + 1$ possible M_J values within each state. Outside of the presence of a magnetic or an electric field, all of these $2J + 1$ states are degenerate. Therefore, for the p^2 electron configuration we have

$^1\text{S}_0$: degeneracy of 1
$^1\text{D}_2$: degeneracy of 5
$^3\text{P}_2$: degeneracy of 5
$^3\text{P}_1$: degeneracy of 3
$^3\text{P}_0$: degeneracy of 1
Total: 15 separate possible states

Thus, there are 15 individual electronic states just within the p^2 electron configuration of a carbon atom. Because of the degeneracies, in most cases we will have only five different energy levels (except in the case of a magnetic or an electric field). Just as an electron configuration is separated into a group, or manifold, of L and S states, so the J quantum number separates each L and S term symbol into a (potential) manifold of individual states, and under the proper conditions each J level separates into its $2J + 1$ different M_J states. This stepwise separation is illustrated in Figure 15.4.

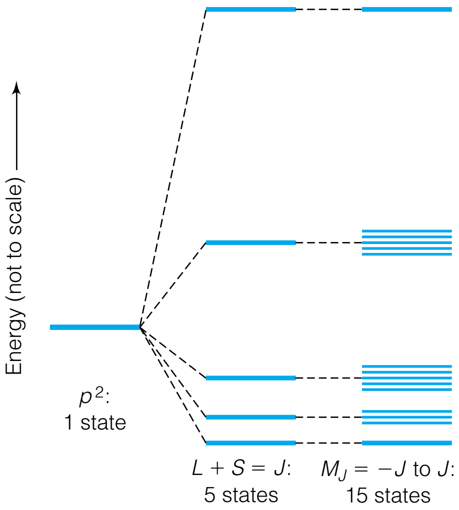

Figure 15.4 The identification of electronic energy levels by J and ultimately M_J quantum numbers. A p^2 electron configuration suggests only a single state. However, the combination of L and S vectors yield 5 different J states which, when separated into M_J states, ultimately yield 15 different states within the p^2 electron configuration. See Figure 15.5 for the term symbols of the 5 states.

Example 15.7

Determine the total number of states in an atom having the electron configuration d^2 for the valence subshell. Use Table 15.1 for the term symbols.

Solution

For the d^2 electron configuration, the term symbols are $^1\text{S}_0$, $^1\text{D}_2$, $^1\text{G}_4$, $^3\text{P}_2$, $^3\text{P}_1$, $^3\text{P}_0$, $^3\text{F}_4$, $^3\text{F}_3$, and $^3\text{F}_2$. There are $2J + 1$ values for M_J for each term, so each state has a degeneracy of 1, 5, 9, 5, 3, 1, 9, 7, and 5, respectively. The total number of states is the sum of these degeneracies, which is 45. There are 45 individual electronic states within the d^2 electron configuration.

These examples might require a rethinking of the idea of excited states. Previously, we have considered an excited state as any state above the ground state, and these excited states have usually been obvious changes in relatively major quantum numbers for the system. In the case of the hydrogen atom, the electronic states have a quantized energy dictated by the principal quantum number n, and the electronic spectrum of hydrogen is due to changes in the n quantum number (and more specifically to concurrent changes in the ℓ quantum number, but this is not immediately apparent because of the degeneracy of the hydrogen electronic states). Moreover, we have used a hydrogen-atom approximation for the labeling of electronic states for multiple-electron atoms, and so we have used the labels 1*s*, 2*s*, 2*p*, and so on for the orbitals of larger atoms.

One might presume, then, that electronic spectra are due to changes in electrons from one orbital to another, as with the hydrogen atom or even the sodium atom discussed above (in that case we were treating the single valence atom of sodium as a hydrogen-like system). However, for atoms with a multi-electron valence subshell, it is more complicated. For such systems, excited states occur *within* the lowest-energy electron configuration. Only one of the term symbols represents the lowest-energy ground state of the atom. The other term symbols are, by definition, excited states. This is despite the fact that all of the states are part of the same electron configuration.

The next question is, then, which of the term symbols represents the ground electronic state? In 1925–1927, after a detailed examination of spectra, Friedrich Hund formulated some rules to determine the term symbol for the ground state. *Hund's rules* are:

1. The term(s) having the higher multiplicity are lower in energy. If this unambiguously determines the term symbol for the ground state, then stop here.
2. Of the term symbols having the highest multiplicity, the higher the value of L, the lower the energy.
3. If the valence subshell is less than half-filled, the *lower* the J, the lower the energy. If the valence subshell is more than half-filled, the *higher* the J, the lower the energy. (Subshells that are exactly half-filled will always have an S term symbol as the highest-multiplicity state and will therefore have only one possible value for J.)

According to these rules, the lowest-energy state for a carbon atom in the p^2 configuration is predicted to be $^3P_0$, which is the case. The $^3P_1$ electronic state is slightly higher in energy (16.4 cm^{-1}), the $^3P_2$ state is slightly higher still (43.5 cm^{-1}). The $^1D_2$ electronic state is much higher in energy (in fact, it is 10,194 cm^{-1} above the ground state), and finally the $^1S_0$ state is the highest-energy state (21,648 cm^{-1} above the ground state) in the manifold of electronic states within the p^2 electron configuration. Figure 15.5 illustrates the different states of this manifold. (Hund's rules are also applicable to molecular electronic states, as we will discuss later in this chapter.)

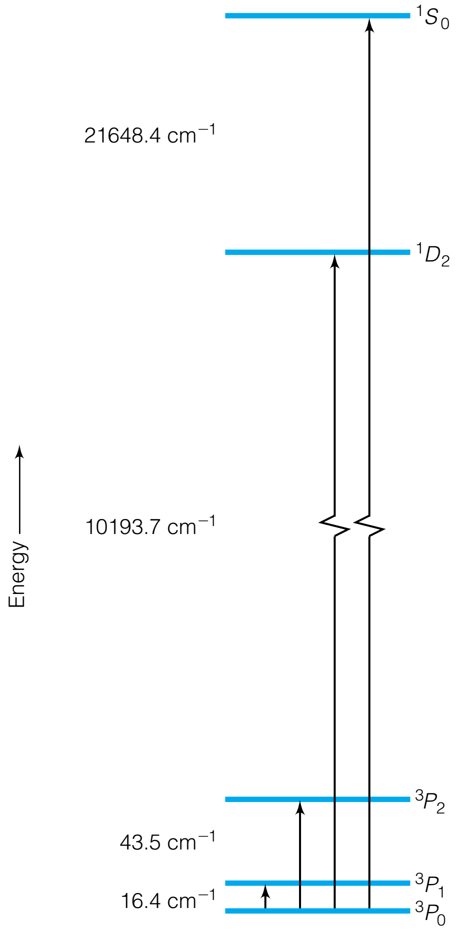

Figure 15.5 Carbon atoms have five distinct electronic energy levels within the $1s^2\,2s^2\,2p^2$ electron configuration, only one of which is the ground state.

Example 15.8

Determine the expected ground state of an atom of Ni, which has a d^8 valence subshell configuration.

Solution

The first step is to recognize that the d^8 electron configuration will have the same term symbols as the d^2 electron configuration, as stated earlier in this chapter. Therefore, we can use the results from Example 15.7 directly. According to Hund's first rule, one of the triplet states will be the ground state. Hund's second rule allows us to choose between the ^{3}P or ^{3}F term symbol by choosing the state having the larger L: the ^{3}F. Finally, Hund's third rule allows us to choose which value of J the ground state will have. Since the d^8 electron configuration represents a subshell that is more than half full, the higher value of J will have the lower energy. Therefore, the $J = 4$ term should be lowest. The term symbol for the ground state of a Ni atom is therefore $^3F_4$.

Example 15.9

Predict the ground-state term symbol for the tetravalent cation of technetium, Tc^{4+}. Assume that its electron configuration has a d^3 valence subshell. Use Table 15.1 for the partial term symbols.

Solution

Of the term symbols for a d^3 electron configuration, the highest multiplicities are 4, for the ^{4}P and ^{4}F states (Hund's first rule). This means that $S = \frac{3}{2}$. The higher of the values of L occurs for the ^{4}F term, so it will be the ground-state term (Hund's second rule). The four values of J in the ^{4}F state are $3 + \frac{3}{2} \rightarrow 3 - \frac{3}{2}$ or $\frac{9}{2}, \frac{7}{2}, \frac{5}{2}$, and $\frac{3}{2}$. For this less-than-half-filled subshell, the lower value of J has the lower energy (Hund's third rule). Therefore, the term symbol of the ground state is $^4F_{3/2}$. (This example illustrates that atomic ions are treated the same way neutral atoms are, and also that values of J can be half-integers. In all cases of an odd number of valence subshell electrons, J will always be half-integral.)

Finally and briefly, term symbols can also be determined for electronic states that have more than one unfilled electronic subshell. For example, the electron configuration $2s^1\,2p^1$ is one possible configuration for an excited state of an He atom. The individual angular momenta of the two electrons ($\ell = 0$, $m_\ell = 0$ and $\ell = 1$, $m_\ell = -1$ or 0 or 1) combine vectorially to give $L = 1$ (the only possible value for L) and $S = 0$ or 1 for ^{3}P and ^{1}P terms. Possible values for J can be determined accordingly. In cases like this, however, the Pauli principle does not exclude certain combinations of angular momenta, because the electrons now have different quantum numbers for angular momentum. If the excited-state electron configuration were $2s^2$, the Pauli principle would eliminate certain term symbols as being impossible.

Because additional labels are necessary to specify electronic states of multielectron valence shells, additional selection rules are necessary to indicate allowed transitions between the states. The previous selection rules, equations 15.4 and 15.5, are not strictly applicable because ℓ and m_ℓ are not considered good quantum numbers. However, there are related (and perhaps not entirely surprising) selection rules in terms of L and S, and now one for J:

$$\Delta L = 0, \pm 1 \tag{15.13}$$

$$\Delta S = 0 \tag{15.14}$$

$$\Delta J = 0, \pm 1 \quad (\text{but } J_{\text{init}} = 0 \longrightarrow J_{\text{final}} = 0 \text{ is forbidden}) \tag{15.15}$$

These three selection rules require several comments. First, a $\Delta L = 0$ transition is possible. This seemingly contradicts our earlier $\Delta \ell = \pm 1$ selection rule, but for multielectron atoms it is possible to have transitions where the change in the approximate ℓ quantum number is $+1$ or -1 while the change in the more rigorous L quantum number is 0. Second, the selection rule $\Delta S = 0$ is useful: electronic energy states that have different multiplicities should not participate in allowed spectroscopic transitions. This allows us to separate electronic spectra on the basis of multiplicity into *systems* that have the same value of S. Allowed transitions can occur only within a system. This fact can be useful when trying to interpret an unknown spectrum. (Recall that this is for allowed electronic transitions. Although transitions where $\Delta S \neq 0$ are technically forbidden, they do occur. Phosphorescence is a process in which such forbidden transitions do occur.)

There is an exception to the selection rule $\Delta J = 0$: an electronic state having $J = 0$ will not participate in an allowed transition with another electronic state that also has $J = 0$. This rule comes from the consideration of the symmetry of wavefunctions for $J = 0$ states, and we will not go into detail about it here. Finally, it should be understood that these selection rules of course apply only to atomic systems where the Russell-Saunders coupling scheme is applicable. For large atoms (approximately $Z > 30$, where Z is the atomic nuclear charge), this coupling system breaks down and the *j-j* coupling system is more appropriate.

Atomic spectra are occasionally displayed diagrammatically in what are called *Grotrian diagrams*, after the scientist Walter Grotrian. Figures 15.6 and

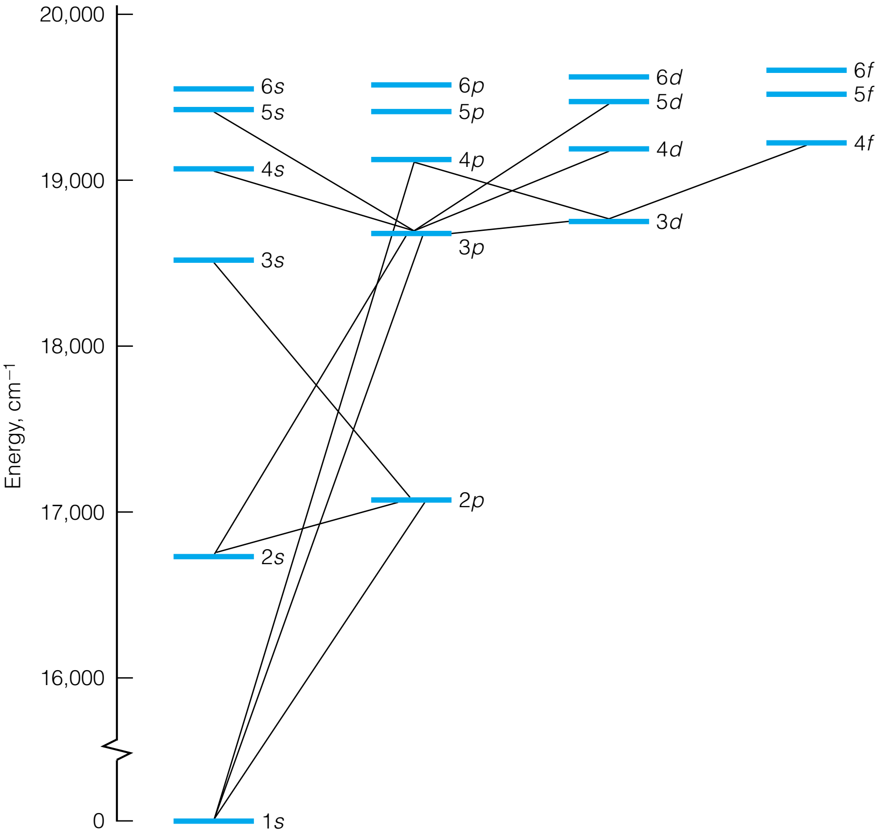

Figure 15.6 A partial Grotrian diagram for helium. Understand that these are not the only possible transitions, only a few. *Source: Physical Chemistry* by Vemulapalli, G. K., © 1993. Adapted by permission of Prentice-Hall, Inc., Upper Saddle River, NJ.

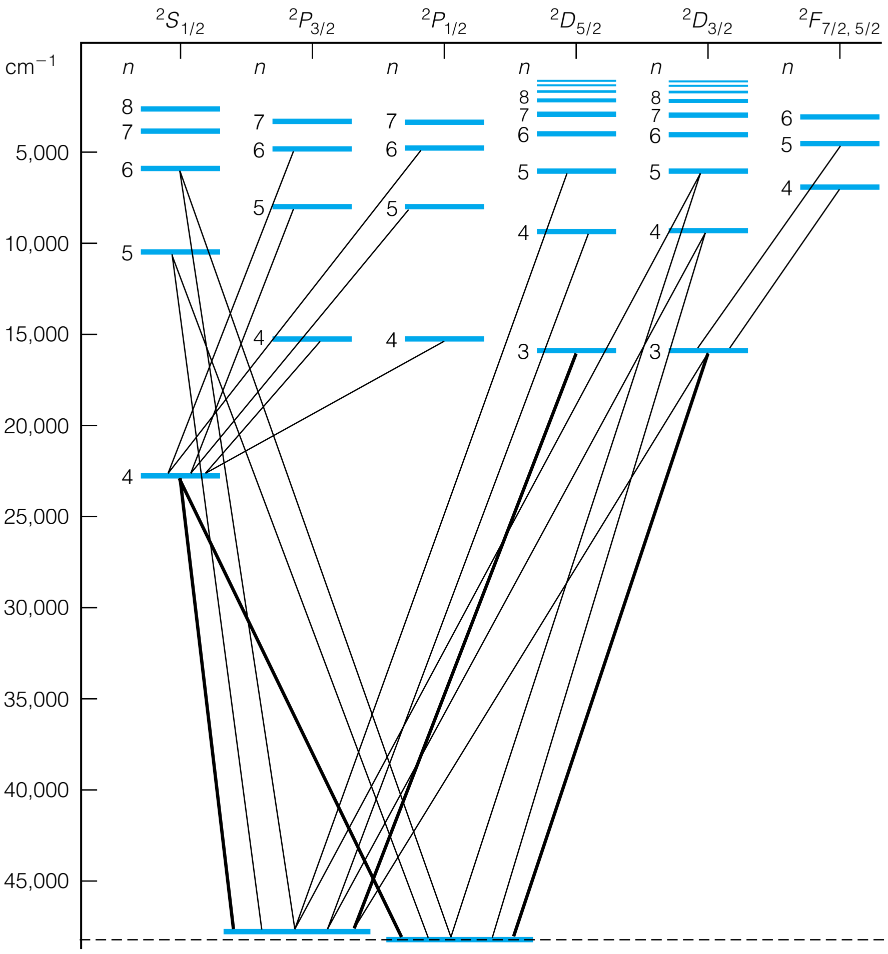

Figure 15.7 A partial Grotrian diagram for aluminum atoms in the gas phase. The thickness of the lines indicates the relative intensity of the electronic transition. *Source:* G. Herzberg, *Atomic Spectra and Atomic Structures,* trans. J. W. T. Spinks, Dover, New York, 1944. Reprinted with permission from the publisher.

15.7 show two Grotrian diagrams, illustrating the allowed transitions. As might be expected, atoms that have more unpaired valence shell electrons have a more complicated Grotrian diagram.

The spectra of atoms can be measured by generating the atoms, for example by vaporizing them into the gas phase. This can be difficult sometimes, especially for a substance like tungsten, which has a normal boiling point of 5660°C. However, many atoms and ions exist in the solid state as either metal complexes or as ionic crystals. Although the imposition of other chemical species around the atom or ion affects the spectrum (this is known as crystal field theory), the previous discussion provides the basis for understanding the electronic transitions of atoms and ions in compounds.

15.6 Electronic Spectra of Diatomic Molecules

The electronic spectra of molecules, even the smallest diatomic molecules, are more complicated than those of atoms because more than one nucleus is present. However, now we can take advantage of molecular symmetry. Just as with vibrational spectroscopy, electronic spectroscopy of molecules uses group-theoretical ideas for simplification. Since all diatomic molecules have either

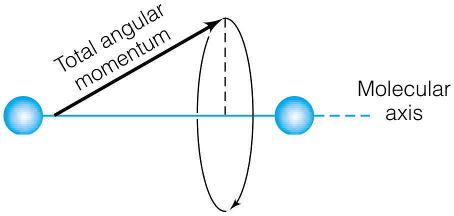

Figure 15.8 Electronic spectra of diatomic molecules are described on the basis of the component of electron angular momentum about the molecular axis, as shown.

$C_{\infty v}$ or $D_{\infty h}$ symmetry, for the present those two point groups will be important. There are also some similarities in electronic spectra and rotational spectra for diatomic molecules, so a review of rotational motions might be useful.

As for atoms, term symbols can be defined for diatomic molecules. The term symbols for diatomic molecules are determined similarly to the K quantum number for diatomic rotations: the term symbol is determined by the total orbital angular momentum of electrons about the internuclear axis. Figure 15.8 shows how this is determined.

The term symbols look very similar to those for atoms, but the quantum numbers involved are given different labels. Instead of ${}^{2S+1}L_J$, the term symbol for diatomic molecules is

$$ {}^{2S+1}\Lambda_{\Omega} \tag{15.16} $$

where Λ, Ω, and S are as illustrated in Figure 15.9. The quantized total angular momentum vector **J** is the combination of the orbital angular momentum of the electrons **L** (note that electrons paired in molecular orbitals contribute no *overall* angular momentum to the total), the spin orbital momentum of the electrons **S** (again, paired electrons contribute no overall spin angular momentum), and the rotational angular momentum of the molecule itself, **R**. With the exception of **R**, which is perpendicular to the axis of the molecule anyway, all of these angular momenta have components that lie along the molecular axis. The axial component of **L** is Λ, the axial component of **S** is Σ, and the axial component of **J** is Ω (see Figure 15.9). These components are quantized, having integer or half-integer (for some cases of **S**) values of $\hbar$, like all angular momenta. It is the values of Λ and Ω, along with **S**, that make up the term symbol. But just as with L for multielectronic atoms, instead of using the numerical value of Λ in the term symbol, a letter is used. Unlike atomic term symbols, diatomic term symbols use capital Greek letters:

Λ	Letter designation
0	Σ
1	Π
2	Δ
3	Φ
⋮	⋮

Care should be taken to not confuse Σ, the quantum number for the axial spin component, with Σ as a term symbol. As with the quantum number J, the

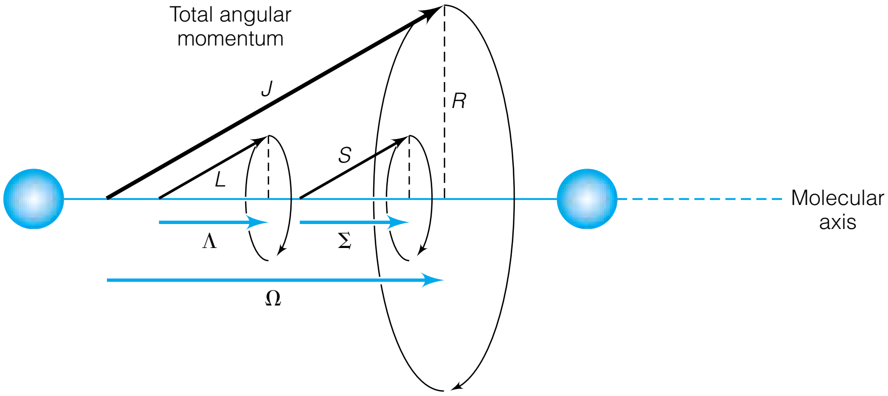

Figure 15.9 Electronic spectra of diatomic molecules are more specifically defined in terms of Λ, Ω, and S. Λ is defined in terms of the orbital angular momentum of the electrons, L. Ω is defined in terms of the total angular momentum, J. The vector difference between L and J is, of course, S.

quantum number Ω may have several possible values depending on the values of Λ and Σ, but now the restriction on negative values of it is lifted:

$$\Omega = \Lambda + \Sigma \longrightarrow \Lambda - \Sigma \quad \text{in integral steps} \tag{15.17}$$

For states other than those having $\Sigma = 0$, the total angular momentum vector can be moving ("precessing") about the internuclear axis in two directions, much the same as the two-dimensional rigid rotor. Therefore, every state with $\Sigma \neq 0$ is at least doubly degenerate.

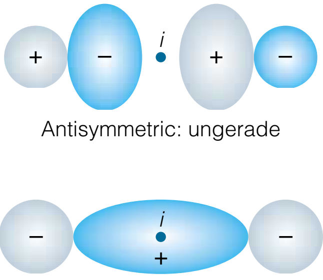

Figure 15.10 Wavefunctions for homonuclear diatomic molecules are labeled gerade or ungerade, depending on the behavior of the wavefunction upon operation by the symmetry element of the inversion center.

For homonuclear diatomic molecules (which have the point group $D_{\infty h}$), an extra label goes on the term symbol. A homonuclear diatomic molecule has a center of symmetry, and wavefunctions can be either symmetric with respect to the center of symmetry, or antisymmetric with respect to the center of symmetry. Figure 15.10 illustrates symmetric and antisymmetric molecular wavefunctions. They are analogous to symmetry and antisymmetry labels for atomic wavefunctions. If a particular electronic state of a homonuclear diatomic molecule is symmetric with respect to the center of symmetry, the label *gerade* (German for "even") is applied and the letter "g" is added as a right subscript in the term symbol. If a particular electronic state is antisymmetric with respect to the center of symmetry, the label *ungerade* (German for "odd") is applied and the letter "u" is added to the term symbol. Figure 15.10 has labeled the example wavefunctions as gerade or ungerade.

Determining term symbols for diatomic molecules follows a procedure similar to that for atoms. Consider O_2 as an example. The molecular orbitals for O_2, derived from the atomic orbitals of each oxygen atom, are shown in Figure 15.11. In the ground state of the diatomic molecule, the unfilled molecular orbitals come from the unfilled subshell of the atoms; in this case, the p^4 electrons. For diatomic oxygen, the unfilled molecular orbitals are the π^* molecular orbital. As a π orbital, this molecular orbital can be assumed to be similar to a p atomic orbital and so would have a single unit of orbital angular momentum. Using the letter λ to designate the orbital angular momentum, this implies that $\lambda_1 = \lambda_2 = 1$. (Here we are using the subscripts 1 and 2 to indicate the individual electron. It does not matter which is 1 and which is 2.) In essence, these two π electrons have angular momenta that couple just like two p electrons, except that now, for molecules, we use lowercase Greek letters to indicate the term symbols. However, unlike in an atom, we have only two degenerate orbitals, not three degenerate orbitals (like we have for atomic p orbitals). In this case, this limits the possible combinations of Λ to $\lambda_1 + \lambda_2$ and $\lambda_1 - \lambda_2$.

There is a different way to consider this coupling, and it becomes useful for polyatomic molecules: use symmetry when possible. Each molecular orbital can be given a symmetry label that is one of the irreducible representations of the molecular point group. In the case of the homonuclear diatomic, the point group is $D_{\infty h}$. As we might expect for a doubly degenerate molecular orbital, the label for these π^* orbitals is Π, but the $D_{\infty h}$ point group requires a label of g or u for each irreducible representation. The diagrams of each molecular orbital in Figure 15.11 show that the π^* orbitals have gerade symmetry with respect to the center of symmetry, so that each one can be labeled as Π_g. The following statement is therefore applicable: the term symbols that label the energy levels of unpaired electrons in a molecule are determined from the direct product of the irreducible representations of the molecular orbitals that contain the unpaired electrons. In this case, this means evaluating

$$\Pi_g \otimes \Pi_g$$

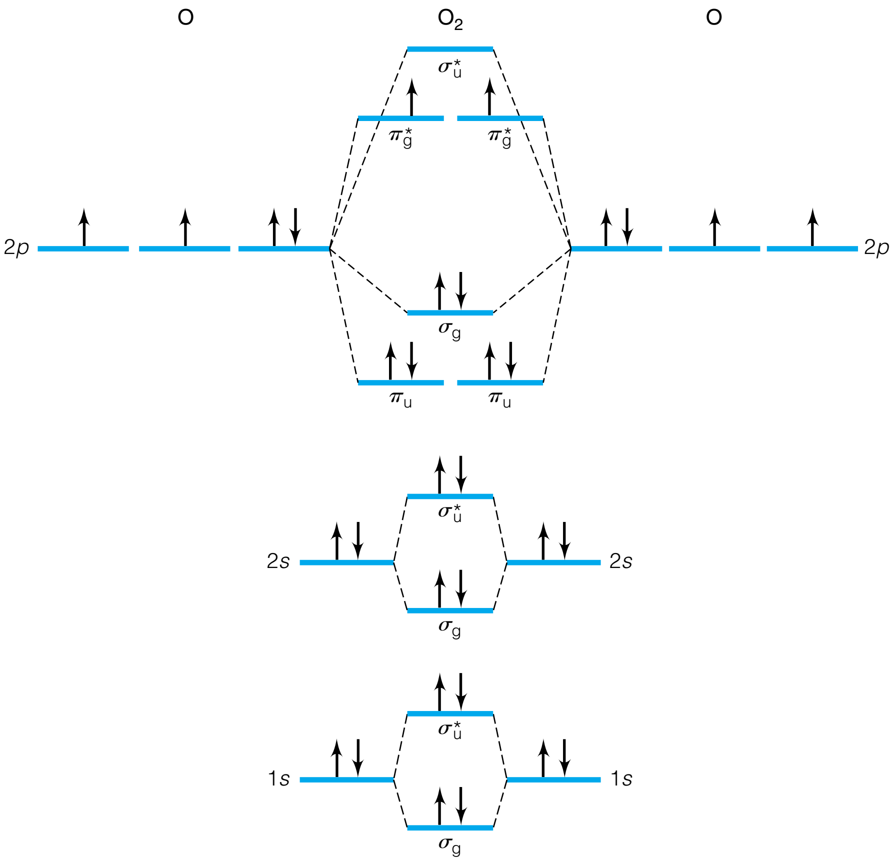

Figure 15.11 Molecular orbitals of O_2. Simple diagrams like those in Figure 15.10 make it easy to determine which orbitals are gerade and which are ungerade.

Because the $D_{\infty h}$ point group has a formal order of ∞, other methods must be used to determine how this direct product reduces. It does reduce to

$$\Sigma_g^+ \oplus \Sigma_g^- \oplus \Delta_g$$

(One way to rationalize this in the absence of the great orthogonality theorem is that there are three possible ways to write the two electrons in two molecular orbitals: (1) separate orbitals, spins same direction, (2) separate orbitals, spins opposite directions, and (3) same orbital, spins opposite directions (they cannot be the same direction due to the Pauli principle). The first two states are singly degenerate. How many ways can you put indistinguishable electrons in the orbitals in the same or different spins? (Recall that we cannot differentiate between "spin up" and "spin down" without a magnetic field.) One way for each spin, therefore two individual Σ (degeneracy = 1) states. However, how many ways can you put the two electrons in a single orbital with different spins? Two ways, because there are *two* different π^* orbitals. Therefore, a doubly degenerate Δ state is needed. The total number of ways? Four, the same as the character of the E symmetry element for a $\Pi \times \Pi$ direct product.

The Pauli principle limits the possible spins for the above term symbols. This is due strictly to the antisymmetry requirement of the Pauli principle. The + and − labels on the sigma (Σ) states in the direct sum above indicate symmetric and antisymmetric spatial symmetry, respectively (specifically, with respect to the vertical reflection planes). Similarly, the Δ term symbol represents a symmetric spatial electronic state (check its character!). Therefore, the symmetric spatial states must be paired with antisymmetric spin states, and antisymmetric spatial states can be paired with symmetric spin states. When this is done, the following term symbols are possible:

$$^1\Sigma_g^+,\ ^3\Sigma_g^-, \text{ and } ^1\Delta_g$$

Hund's rules are applicable to molecular electronic states as well as atomic electronic states (which is partly why they are so useful). Therefore, the highest-multiplicity electronic state, the $^3\Sigma_g^-$ state, is predicted to be the ground state. (It is, as determined experimentally by various means.) The $^1\Sigma_g^+$ and $^1\Delta_g$ electronic states are excited states within the $(\pi^*)^2$ electronic configuration of the diatomic molecule (see Figure 15.11).

Example 15.10

Predict the term symbol(s) of the ground electronic configuration of an excited state of oxygen that has one of its electrons in the σ^* antibonding orbital. See Figure 15.11 for assistance in determining the symmetry label of the excited electron. Note that you need not know all of the characters of the irreducible representation to determine the necessary characters of the direct product.

Solution

The excited electron in the σ^* antibonding orbital is in a molecular orbital that has Σ_u^+ symmetry, and the electron still in the π^* orbital has Π_u symmetry. The direct product of these two symmetries is simply Π_u. (Verify this.) The σ^* and π^* electrons can have either the same direction spin or different direction spin (rather, the z components of their spin), so multiplicities of 3 or 1 are possible. Therefore, the term symbols for this excited-state electron configuration are $^3\Pi_u$ and $^1\Pi_u$. Π states are doubly degenerate. In this case, there are two possible, degenerate π^* molecular orbitals for the unexcited electron. Complete term symbols would have values for Ω included. For the triplet state, Ω can be 2, 1, or 0. For the singlet state, Ω can only be 1. Unlike atomic term symbols, it is relatively uncommon to see the Ω values listed explicitly in the term symbols of diatomic molecules. One would see $^3\Pi_u$ to represent all three individual states, rather than $^3\Pi_{u,2}$, $^3\Pi_{u,1}$, and $\Pi_{u,0}$.

Now we need to consider selection rules. The following rules are applicable to diatomic molecules only. For allowed electronic transitions:

$$\Delta\Lambda = 0, \pm 1 \tag{15.18}$$

$$\Delta S = 0 \tag{15.19}$$

$$\Delta\Omega = 0, \pm 1 \tag{15.20}$$

$$\text{g} \longleftrightarrow \text{u (for homonuclear diatomics)} \tag{15.21}$$

$$\text{For } \Sigma \text{ states, } + \longleftrightarrow +,\ - \longleftrightarrow -, \text{ but } \textit{not } + \longleftrightarrow - \tag{15.22}$$

where in equations 15.21 and 15.22, an arrow means that states having this change in label (ungerade to gerade, or gerade to ungerade) are allowed. These selection rules are qualitatively similar to the selection rules for atoms. Note once again a restriction on the allowed change in the S quantum number: no change is allowed. This is the case for diatomic molecules having small atoms.

As coupling of the angular momenta increases with atomic number, more and more "forbidden" transitions are observed in the electronic spectra.

Example 15.11

Given that the ground state of O_2 is $^3\Sigma_g^-$, list the term symbols of the electronic states that can be accessed by allowed electronic transitions. Do not consider the changes in Ω.

Solution

A Σ state means that its Λ value is 0, so possible excited states can have $\Lambda = 0$ or 1, which will be Σ or Π states. A multiplicity of 3 means that $S = 1$, and since $\Delta S = 0$ the excited states will also have an S of 1 and a multiplicity of 3. Since the ground state is gerade, the excited states must be ungerade. Therefore, possible allowed excited states are $^3\Sigma_u^-$ and $^3\Pi_u$. Note the $-$ sign on the Σ state.

15.7 Vibrational Structure and the Franck-Condon Principle

Recall that, generally, electronic states are separated by more energy than are vibrational states (which are in turn separated by more energy than are rotational states). It is common to consider that every electronic state of a molecule has its own collection, or *manifold,* of vibrational states. The following discussion is easiest if one assumes a diatomic molecule (although the ideas are applicable to all molecules).

When a molecule absorbs a photon that excites an electron to a higher-energy state, the state of the molecule is described by a different wavefunction. For the ground-state wavefunction, a diatomic molecule has a certain equilibrium bond distance. Even though it is probably vibrating in its lowest vibrational quantum state (recall the existence of zero-point energy for quantized vibrations), it is presumably vibrating about an average bond distance known as the *equilibrium bond distance.* It is usually labeled R_e or r_e.

An excited-state electronic wavefunction is similar. It too has its own lowest vibrational quantum state and equilibrium bond distance. However, there is no guarantee that the equilibrium bond distances will be the same. Normally, equilibrium bond distances change with electronic state. This is illustrated in Figure 15.12, which shows two electronic states, their respective vibrational state manifold, and an energy minimum that occurs at different internuclear distances.

If these two states are involved in an allowed transition, there are several considerations. First, a Born-Oppenheimer type of approximation is applicable in that an electronic transition occurs so fast (on the order of 10^{-15} s[†]) that the nuclei do not have time to move: that is, translations and vibrational and rotational motions do not occur on the timescale of electronic transitions. On a diagram such as Figure 15.12, a system in its ground electronic state would move to an excited state by *moving straight up in the figure.* This means that the internuclear distance does not change. This idea is called the *Franck-Condon principle.* (It is named after the German physicist James Franck and

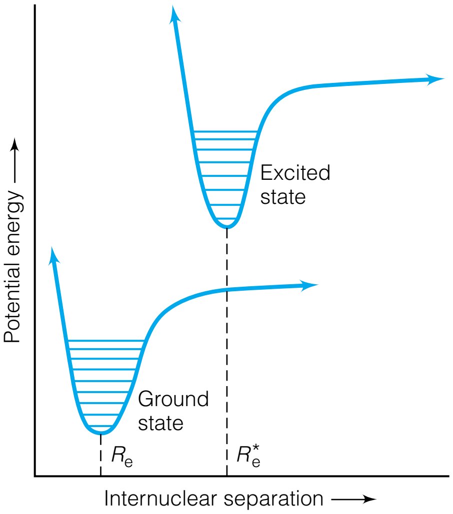

Figure 15.12 Different electronic states have different minimum-energy internuclear distances as well as different vibrational energy manifolds within each. This complicates the electronic spectra of even the simplest, diatomic molecules.

[†] Compare this to a single vibration of an H_2 molecule, which lasts ~8×10^{-15} s, or 8 fs.

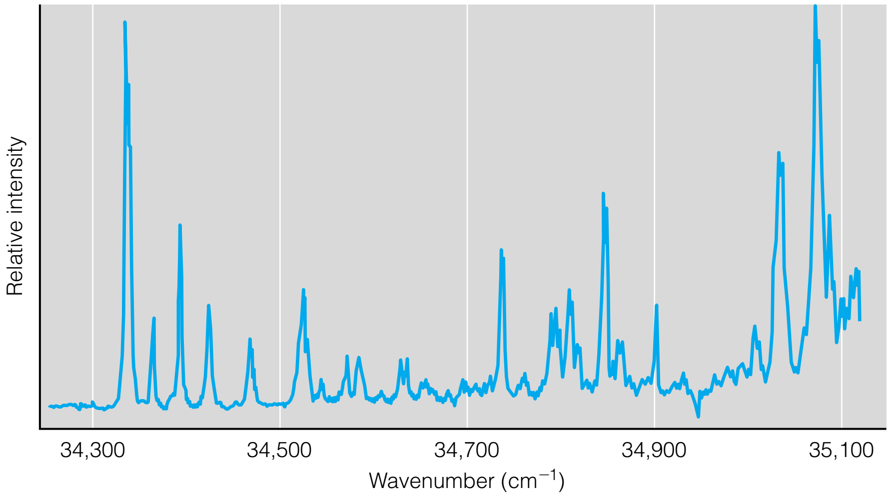

Figure 15.13 A high-resolution electronic spectrum of methylaniline, showing a pattern of lines that is attributable to different vibrational energy levels involved in the electronic transition. *Source:* B. Ballesteros and N. Santos, *Spectrochim. Acta, Part A,* 2002, 58: 1074.

the American physicist Edward U. Condon. Franck shared a 1925 Nobel Prize for his work on the interactions between electrons and atoms. Among other things, Condon worked on the Manhattan Project to develop the nuclear bomb.) The law of conservation of momentum can be used to justify the Franck-Condon principle. Since momentum equals $m \cdot v$, the velocity of the atoms must be very close in both states in order for a transition to occur (since masses of the atoms are constant). Molecules whose atoms are moving very quickly will experience transitions to (vibrational) states in which the atoms are also moving quickly. Molecules whose atoms are almost at rest (like at the turning point of a vibration) will experience transitions to higher vibrational states in which atoms in the excited state are also almost at rest.

A second consideration in electronic spectra is the recognition that electronic states, usually separated by a relatively large amount of energy, have within each of them a vibrational manifold of states. High-resolution electronic spectra such as the one shown in Figure 15.13 reveal a set of lines superimposed on the transition. These lines represent different initial and final *vibrational* states of the molecules within the initial and final electronic states. Such transitions are referred to as vibrational-electronic, or *vibronic,* transitions. In vibronic spectra, the selection rules for the electronic transition are given in equations 15.18 to 15.22 (for diatomic molecules). However, there are no specific selection rules for what vibrational states can participate in the vibronic transition. This is because the vibrational selection rule, $\Delta v = \pm 1$, is applicable only for harmonic-oscillator vibrations within a *single* electronic state. It is not applicable to vibrational wavefunctions from differing electronic states. *Any* vibrational transitions can participate in a combined vibrational-electronic transition.

However, not all of them will, and it is the Franck-Condon principle that justifies the participation of various vibrational levels in a vibronic spectrum. The Franck-Condon principle requires that an electronic transition be represented by a *vertical* move in a diagram such as Figure 15.14. In order for such a transition to be considered likely, not only must the two particular vibrational states overlap each other vertically, but the overlap must include parts of the vibrational wavefunctions that have similar probability. Figure 15.14 shows

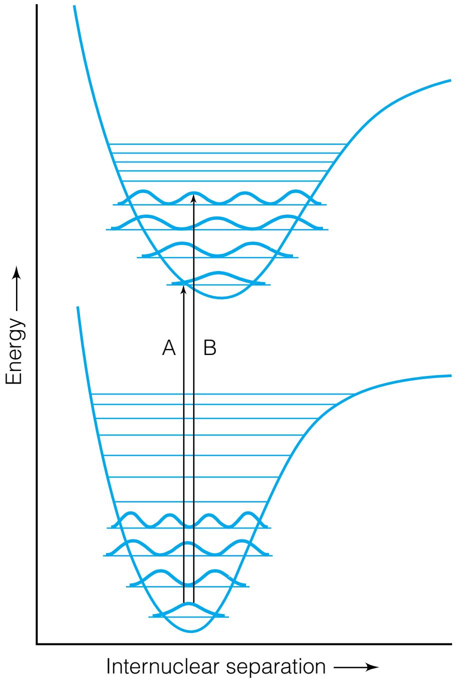

Figure 15.14 Two examples of electronic transitions that have different probabilities due to the Franck-Condon principle. The transition labeled A has a low probability, because it is going from a maximum probability in the ground-state vibrational wavefunction to a minimum probability in the excited-state vibrational wavefunction. The transition labeled B has a higher probability, because it involves two vibrations of more similar probability at that particular internuclear separation.

two examples of a high-probability and a low-probability transition using Franck-Condon principles. The transition marked A has a low probability, because the vibrational wavefunctions do not overlap well, and a high-probability region is in the same nuclear position as a low-probability region. The transition marked B has a higher probability because high probabilities overlap.

Mathematically, the transition moment of a vibronic transition depends on an overlap integral in terms of the electronic *and vibrational* wavefunctions. The form of the transition moment is

$$M = \int \Psi^*_{\text{el,upper}}\Psi^*_{\text{vib,upper}}\hat{\mu}\Psi_{\text{el,lower}}\Psi_{\text{vib,lower}}\, d\tau \tag{15.23}$$

where the "el" refers to the electronic wavefunction and "vib" refers to the vibrational wavefunction. The operator $\hat{\mu}$ is the electric dipole operator. Since the change in the molecule involves one of its electrons, to a good approximation the dipole moment operator affects the electronic wavefunction and not the vibrational wavefunction. The above integral can therefore be separated as

$$M = \int \Psi^*_{\text{el,upper}}\hat{\mu}\Psi_{\text{el,lower}}\, d\tau \int \Psi^*_{\text{vib,upper}}\Psi_{\text{vib,lower}}\, d\tau \tag{15.24}$$

The first integral represents a "normal" transition moment. The value of the second integral is not determined by orthonormality, since it represents different vibrational wavefunctions of *different* electronic states. This second integral is known as the *Franck-Condon overlap integral,* and it is a measure of the amount of overlap between two different vibrational wavefunctions. The larger the overlap (see Figure 15.14), the larger the transition probability.

The Franck-Condon principle is applicable to polyatomic molecules also. However, as might be expected, the potential energy diagrams get more complicated, in part because there are now $3N - 6$ vibrational degrees of freedom and therefore $3N - 6$ potential energy diagrams to consider for *each* electronic state. Many electronic spectra are actually vibronic spectra. In some electronic spectra, the vibrational structure is visible, in others it is not resolved. Figure 15.15 shows an example of an electronic spectrum at low resolution, so no vibrational structure is seen. Compare this with Figure 15.13, which is a much higher resolution spectrum. See the difference?

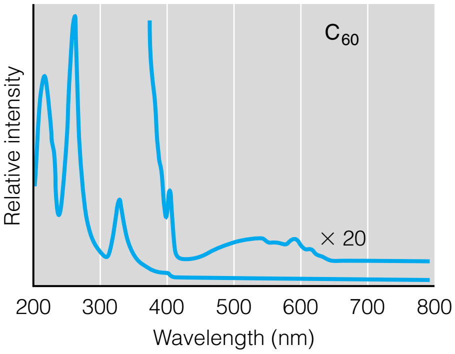

Figure 15.15 Many electronic transitions have vibrational structure, which shows up only under a high resolving power. Compare the low-resolution electronic spectrum of C_{60} with the higher-resolution spectrum of methylaniline in Figure 15.13. *Source:* H. Ajie et al., *J. Phys. Chem.,* 1990, 94: 8633.

15.8 Electronic Spectra of Polyatomic Molecules

Since most chemical species are polyatomic molecules, a discussion of the electronic spectra of molecules covers most matter. However, the subject is so large (the saying "books are written about it" is especially true here) that we can cover only a few specific topics.

The electronic states of polyatomic molecules can be labeled using the irreducible representations of the symmetry point group of the molecule. (This is another example of how symmetry is important in the understanding of spectra.) As such, the same rule involving the direct product of the irreducible representations applies:

$$\Gamma^*_{\text{upper}} \otimes \Gamma_{\text{operator}} \otimes \Gamma_{\text{lower}} \subset A_1 \tag{15.25}$$

or whatever label is the totally symmetric irreducible representation in that symmetry point group. Here, Γ^*_{upper} is the (complex-conjugated) irreducible representation of the upper electronic state, Γ_{lower} is the lower electronic state, and Γ_{operator} is the irreducible representation of the appropriate dipole moment operator. The irreducible representation labels of the dipole moment operator are usually given in the character table, as discussed in the previous chapter regarding allowed vibrational transitions.

For polyatomic molecules, the point group has enough symmetry elements (or rather, classes, and so therefore irreducible representations) that the following statement is usually applicable: the ground electronic state and the allowed excited states are *usually* of different irreducible representation labels.

There are some general rules for electronic spectra of molecules (although exceptions to such rules are not uncommon). For most molecules that are composed of atoms of main-group elements that have an electron configuration with a saturated valence shell, most of the low-energy electronic transitions are already relatively high in energy and already require UV light (that is, higher energy than visible light) for an allowed transition. This is why molecules such as water, ammonia, methane, and so on are colorless. They do not absorb visible light because the electronic transitions are caused by invisible UV light.

In molecules that have an atom with an unpaired electron, there is a good chance that relatively low-energy visible light is energetic enough to cause an electronic transition. An example is NO_2, a rare case of a stable main-group compound that has an odd number of electrons. It is brown, and is largely responsible for the color of smog. This idea is particularly applicable to compounds that contain *d*-block or *f*-block elements: transition, lanthanide, and actinide atoms. Consider compounds that have a Cu^{2+} ion in them. Such an ion has the valence shell electron configuration $3d^9$. There is a single unpaired electron. Therefore, one would predict that Cu^{2+} compounds are colored, and they usually are. However, consider Zn^{2+}. It has a valence shell electron configuration of $3d^{10}$, having no unpaired electrons. Zinc compounds are not known for their colors. (Yes, it is understood that these examples are ions, not molecules. They are simple examples, and since such cations are never present without an anion, we are not stretching the definition *too* much.)

Example 15.12

Predict whether the following molecules would have color. That is, will electronic transitions occur in the visible region of the spectrum, or will they probably occur in the invisible UV region of the spectrum? State the reason(s) why.

a. Sodium chloride, NaCl

b. Iron pentacarbonyl, $Fe(CO)_5$ (Consider the ligands and the metal atom separately.)

c. Chloroform, $CHCl_3$

d. Titanium dioxide, TiO_2

e. Hemoglobin, which has four iron atoms in it

Solution

a. Both the sodium ion, Na^+, and the chloride ion, Cl^-, have an octet electron configuration for the valence shell. All the electrons are paired, so one would expect that sodium chloride would not absorb in the visible region of the spectrum. Crystalline NaCl is colorless and can be used for optical components.

b. Although the ligands have all-paired electrons, the neutral iron atom has a $3d^6$ electron configuration, so one might predict that iron pentacarbonyl would absorb in the visible region of the spectrum. Iron pentacarbonyl is a volatile liquid at room temperature and has a yellow color.

c. All of the atoms in chloroform have complete valence shells and all-paired electrons. This suggests a colorless compound. It is a colorless liquid. (Although it sometimes has a yellowish tinge, it is generally recognized as colorless.)

d. Ti in the 4+ oxidation state has a noble-gas electron configuration, as do the O^{2-} ions. Therefore, this compound is not expected to absorb visible light. Its electronic transitions are expected to occur in the ultraviolet region of the spectrum. TiO_2 is very white. It is extensively used in industry as a white pigment in everything from paints to various food products. (Does it surprise you that you occasionally eat an ingredient of paint?)

e. With four transition metal atoms, it might be expected that hemoglobin is colored. It is responsible for the red color of red blood cells.

15.9 Electronic Spectra of π Electron Systems: Hückel Approximations

It is difficult to state generalities about the electronic structure of molecules, because molecules are so diverse. However, for one group of electrons, there is a relatively easy framework in which to understand electronic energy levels: π electrons in organic molecules. In particular, we are limiting the following discussion to molecules that have alternating single and double bonds; that is, they have *conjugated* π bonds. In organic molecules, π electrons reside in molecular orbitals formed by the side-on, nonaxial overlap of atomic orbitals of the carbon atoms, as shown in Figure 15.16. Such orbitals represent a particularly important aspect of carbon-carbon bonding in organic chemistry. The chemistry of aromatic organic compounds, which are based on benzene, is in part dictated by the electrons located in conjugated π orbitals. Nonaromatic conjugated π electron systems, like 1,3-butadiene, are also relevant molecular systems. (Recall from organic chemistry that conjugated π bonds, alternating single and double carbon bonds, have a special stability since adjacent double bonds can overlap with each other, extending the π electron system. See Figure 15.16 for an illustration.)

—C═C—C═C—C═C—

Figure 15.16 Conjugated π bonds are formed when alternating single and double bonds between carbon atoms overlap, allowing the π electrons to traverse the entire span of the double bonds, instead of being confined between two particular carbons.

An approximate treatment of π electron systems was introduced in 1931 by Erich Hückel and is called the *Hückel approximation* of π orbitals. The first step in a Hückel approximation is to treat the sigma bonds separately from the pi bonds. Therefore, in a Hückel approximation of a molecule, only the π bonds are considered. The usual assumption is that the σ bonds are understood in terms of regular molecular orbital theory. The σ bonds form the overall structure of the molecule, and the π bonds spread out over, or *span,* the available carbon atoms. Such π bonds are formed from the side-on overlap of the carbon 2*p* orbitals. If we are assuming that the π bonds are independent of the σ bonds, then we can assume that the π molecular orbitals are linear combinations of only the 2*p* orbitals of the various carbon atoms. [This is a natural consequence of our earlier linear combination of atomic orbitals—molecular orbitals (LCAO-MO) discussion.] Consider the molecule 1,3-butadiene (Figure 15.17). The π orbitals are assumed to be combinations of the 2*p* atomic orbitals of the four carbon atoms involved in the conjugated double bonds:

$$\Psi(\mathrm{MO}) = c_1\Psi_{2p,\mathrm{C1}} + c_2\Psi_{2p,\mathrm{C2}} + c_3\Psi_{2p,\mathrm{C3}} + c_4\Psi_{2p,\mathrm{C4}}$$

where c_1, c_2, c_3, and c_4 are the expansion coefficients and C1, C2, C3, and C4 refer to the individual carbon atoms. The combination of four atomic orbitals

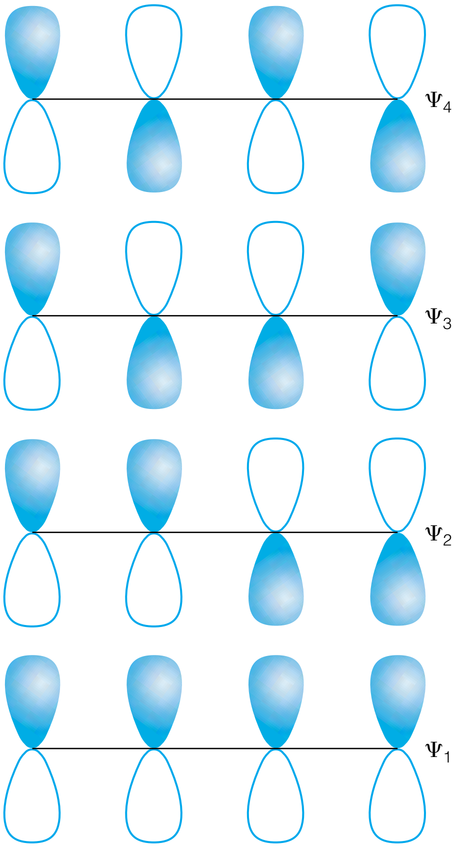

Figure 15.17 The π orbitals of butadiene. Ψ_1 and Ψ_2 are occupied in the ground electronic state (see Figure 15.18).

implies four molecular orbitals, each with its own characteristic values for c_1, c_2, c_3, and c_4, and each with its own energies. Recognize that with two electrons in each molecular orbital, only the two lowest π molecular orbitals for butadiene will be filled. The other two will be empty (and will be considered excited states of butadiene). Linear variation theory (see section 12.8) indicates that the energies can be determined from the following secular determinant:

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} \end{vmatrix} = 0$$

which yields a polynomial having E^4 as the highest power (and hence yields four roots). H_{xy} and S_{xy} are the normally defined energy integrals, respectively, and overlap integrals between carbon x and carbon y:

$$H_{xy} = \int \Psi_x^* \hat{H} \Psi_y \, d\tau$$

$$S_{xy} = \int \Psi_x^* \Psi_y \, d\tau$$

as defined in equation 12.28. Since the atomic orbitals used in the expansion are assumed to be normalized, $H_{11} = H_{22} = H_{33} = H_{44}$, and the value of that energy integral is usually designated by the Greek letter α. Also, the overlap integrals S_{11}, S_{22}, S_{33}, and S_{44} are exactly 1. At this point, no other simplification can be made without approximating a solution.

Hückel put forth some simplifying assumptions. For a Hückel approximation:

1. All other overlap integrals S_{xy} are zero.
2. All energy integrals H_{xy} between nonneighboring atoms are zero.
3. All energy integrals H_{xy} between neighboring atoms have the same value. This value is usually designated by the Greek letter β.

When these assumptions are made, the above 4 × 4 determinant takes the following form (where the values for H_{11}, H_{22}, . . . , and S_{11}, S_{22}, . . . , have also been substituted):

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0$$

This is a much simpler determinant to solve (even if it does still lead to a polynomial having a fourth power of E). It is called the *Hückel determinant* for the π molecular orbitals. The polynomial one gets, when all common terms are collected, is $(\alpha - E)^4 - 3(\alpha - E)^2\beta^2 + \beta^4 = 0$. Algebraic techniques for finding solutions to such equations eventually provide the following four possible values for E: $\alpha - 1.618\beta$, $\alpha - 0.618\beta$, $\alpha + 0.618\beta$, and $\alpha + 1.618\beta$. These states are illustrated graphically in Figure 15.18. By convention, α and β are negative, so the lower-energy states have the + sign and the higher-energy states have the − sign. The four π electrons in butadiene reside in these molecular orbitals in Hund's-rule fashion: two in each orbital, opposite spins. The highest-energy molecular electronic state that has an electron in it is called the *highest occupied molecular orbital*, or HOMO. The lowest-energy molecular electronic state that has no electron in it (when the molecule is in its overall ground electronic state) is called the *lowest unoccupied molecular orbital*, or LUMO. The lowest-energy π electronic transition of a π-electron-containing

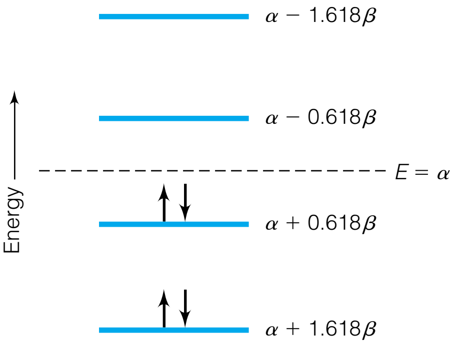

Figure 15.18 Hückel theory predicts this arrangement for the four π electrons in butadiene. A comparison (see text) suggests that this molecule is more stable than expected due to the conjugation of the π electrons.

molecule is the HOMO → LUMO transition, which may or may not be an allowed transition. (It usually is, so the HOMO and LUMO are important in the electronic spectra of such molecules.)

Example 15.13

Perform a Hückel approximation treatment of ethylene, $CH_2{=}CH_2$.

Solution

This treatment is much simpler than butadiene, because only two carbon atoms are involved. It should be easy to apply Hückel's approximations to get the following 2 × 2 Hückel determinant:

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

Upon multiplying out the terms in the determinant, one gets

$$(\alpha - E)^2 - \beta^2 = 0$$

$$(\alpha - E)^2 = \beta^2$$

$$(\alpha - E) = \pm\beta$$

$$E = \alpha \pm \beta$$

for the two electronic π orbitals in ethylene. They are illustrated in Figure 15.19, with the lower of the two orbitals having energy $\alpha + \beta$. This is the HOMO of ethylene. The LUMO of ethylene has an energy of $\alpha - \beta$. The electronic spectrum of ethylene has an absorption at about 2000 Å that has been assigned to the transition between the HOMO and LUMO.

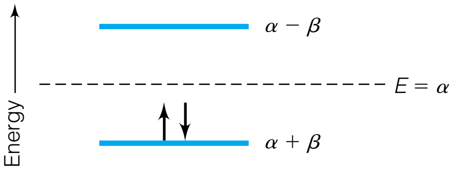

Figure 15.19 Hückel theory predicts the above arrangement for the two π electrons in ethylene.

If we compare the answers for ethylene and for butadiene, there is a slight difference from what we might expect. (Ethylene has the simplest π electron system, so comparisons to its energy levels are common.) If butadiene were just two ethylenic systems, then the energies of the four π electrons should be simply $4(\alpha + \beta) = 4\alpha + 4\beta$. However, as seen above, the total energy of the four butadiene electrons, which occupy the two lowest-energy electronic states, is $2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) = 4\alpha + 4.472\ \beta$, or 0.472β lower in energy than expected. (Recall that β itself is negative.) This lower total energy is due to the fact that the π electrons in butadiene are not confined to a single double bond (a situation termed "localized") but have some probability of being found along the entire length of the conjugated system (they are "delocalized"). This extra energy stability of the four π electrons of butadiene, 0.472β, is called the *delocalization energy* of the π electron system.

Values of α and β are measured spectroscopically, and the electronic spectroscopy of many π electron systems shows that the Hückel approximation works fairly well. Many transitions between π electronic states occur in the visible or ultraviolet region of the spectrum. These transitions are the cause of color in conjugated π electron systems. In the Hückel approximation, all of the π molecular orbitals end up with a value of energy having the form $E = \alpha + K\beta$, where the value for K depends on the system. Therefore, only the values of K and β determine the molecule's π energy level pattern, which is what is probed in an experimental spectrum. However, because of how it is defined, β has a similar value for most π systems: about −75 kJ/mol. The value for α can be determined from atomic spectra. Since a specific value for α is not necessary in understanding the *pattern* of the π electronic states, its value is not usually a matter of concern. (For carbon atoms, α is about -1120 kJ/mol, which is much larger than β.)

15.10 Benzene and Aromaticity

The Hückel approximation is especially useful in understanding the chemical stability of benzene, and by extension other aromatic compounds. Recall that benzene (Figure 15.20) is more stable than expected for a "cyclohexatriene," and its chemistry is representative of an entire class of aromatic hydrocarbons

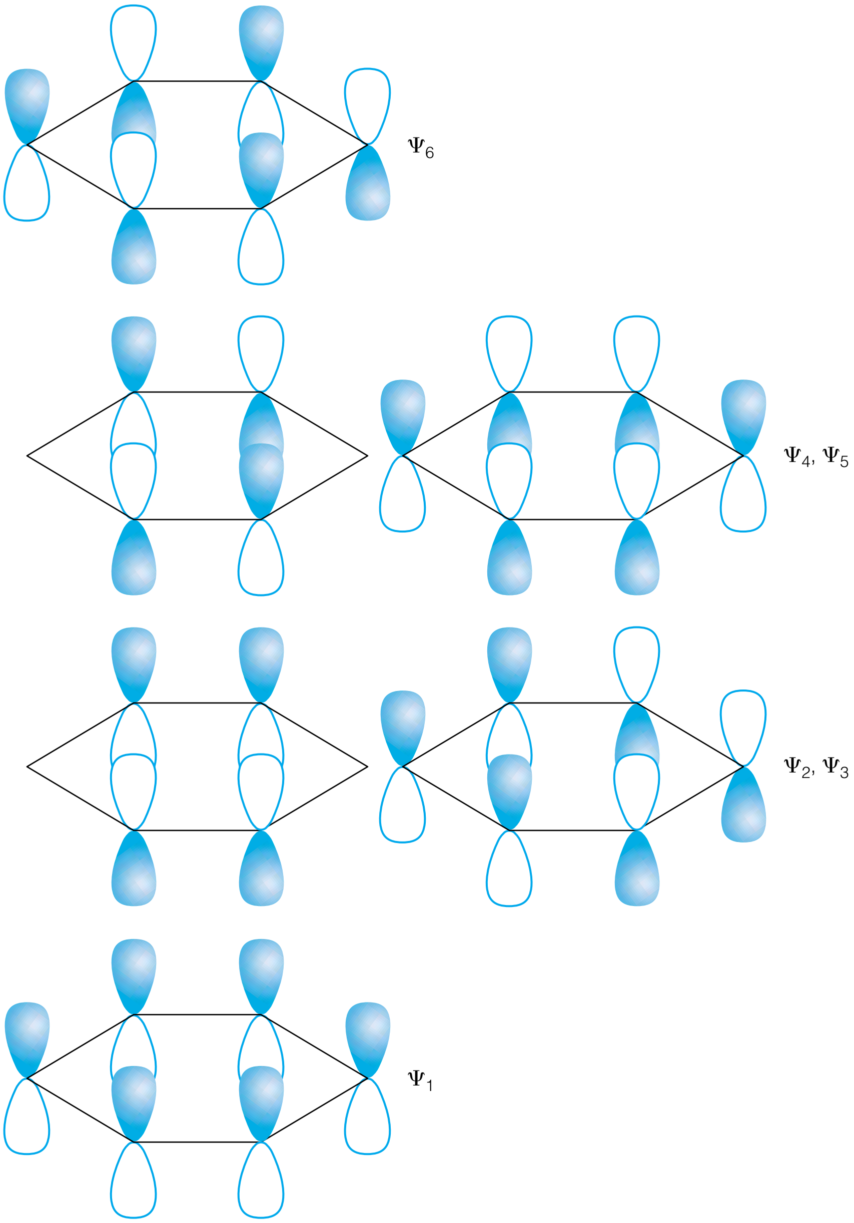

Figure 15.20 The π orbitals of benzene. Ψ_1 and the degenerate pair Ψ_2 and Ψ_3 are occupied in the ground electronic state (see Figure 15.21).

as opposed to the nonaromatic aliphatic hydrocarbons. The Hückel approximation provides some clues for benzene's distinctions.

Benzene has six carbon atoms arranged in a ring, each contributing one *p* electron to the π molecular orbitals. Therefore, the 6 × 6 determinant constructed using Hückel's approximations looks like this:

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \quad \textbf{(15.26)}$$

The only real difference between equation 15.26 and the earlier Hückel determinants is the presence of β in the upper right and lower left corners. This is because the molecule is cyclic and the first carbon atom is adjacent to the sixth carbon atom.

Evaluating the above determinant requires solving a polynomial that is sixth order in E (that is, the highest power of E in the polynomial is E^6). Upon solving for the values of E in terms of α and β (which will not be shown here), one finds the following values for E: $\alpha + 2\beta$, $\alpha + \beta$, $\alpha + \beta$, $\alpha - \beta$, $\alpha - \beta$, and $\alpha - 2\beta$. Two of the energies, $\alpha + \beta$ and $\alpha - \beta$, are also doubly degenerate. An energy level diagram of these molecular orbitals is shown in Figure 15.21, along with the six π electrons in the three lowest orbitals.

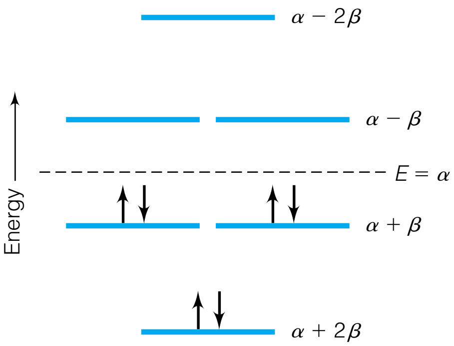

Figure 15.21 Hückel theory predicts the above arrangement for the six π electrons in benzene. The amount of additional stability in the π orbitals of benzene is so great that it defines aromaticity.

There are two points about the π orbitals of benzene. First, all of the net "bonding" orbitals (the orbitals having lower energy than the 2*p* electrons in the carbon atom, which have an energy of α) are completely filled. Therefore, the benzene molecule experiences the *maximum possible decrease* in overall energy—and therefore the maximum possible increase in stability—that it can. (Indeed, it is somewhat akin to the diatomic nitrogen molecule, which has three pairs of electrons in bonding molecular orbitals.) Therefore, we expect that benzene should be more stable than expected, and it is. Second, consider the delocalization energy. The total energy of the six π electrons is $2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$. Compare this to three units of ethylene (the system against which all delocalization energies are compared), which for the six π electrons would have a π electron energy of $6(\alpha + \beta) = 6\alpha + 6\beta$. Benzene therefore has 2β more of a decrease in energy, representing a delocalization energy of approximately 150 kJ/mol. This is more than four times the delocalization energy of butadiene, which at 0.472β of delocalization energy represents a decrease in energy of only ~35.4 kJ/mol. Benzene is much more stable than expected simply on the basis of having three double bonds! This unexpected (but explainable, in terms of the Hückel approximation) stability of benzene is given a name: *aromaticity.* Benzene is *aromatic.* The name was derived from the pungent odors of benzene and benzene-related compounds. It now specifically refers to the increased stability of certain cyclic π-electron-containing compounds.

Benzene is not the only aromatic compound. That is, six-membered rings with (nominally) three alternating double bonds are not the only systems that display the more-stable-than-expected character of aromaticity. A range of Hückel determinants can be examined and a rule of thumb derived in terms of maximal filling of bonding π orbitals. It is found that planar cyclic molecules that have 2, 6, 10, 14, . . . , π electrons have all such electrons in lower-energy bonding molecular orbitals and therefore are considered aromatic like benzene. This generality is called the *4n + 2 rule,* where *n* is any nonnegative integer and the expression $4n + 2$ yields the number of π electrons in the system. (For example, $n = 1$ predicts 6 π electrons, which is what is found for benzene.) The rule is of limited value, because in large molecules the deviation from planarity is large. However, it is useful for predicting whether or not heterocyclic compounds (that is, cyclic compounds that have atoms other than carbon) or ions composed of cyclic carbon rings will be unusually stable.

The ultraviolet spectrum of benzene (and other aromatic compounds) is dominated by transitions of the π electrons from the lower π orbitals to the higher-lying, normally unoccupied π orbitals. A strong absorption occurring at ~1800 Å marks the beginning of such transitions. (The electronic spectrum of benzene has absorptions at lower energies, corresponding to light having wavelengths of ~2600 Å. Such absorptions were historically very well known and are one of the earliest recognized examples of transitions involving an electronic transition that is formally forbidden but made allowed by the vibrations of the molecule.

The *extended Hückel method* for molecular orbitals includes a treatment of all valence electrons (σ and π), not just the π electrons. Atomic orbitals from atoms are used to determine molecular orbital energies by defining the integrals H_{xy} and S_{xy} in a fashion similar to that just presented for the π electrons. Although similar in principle, it requires larger matrices because all valence electrons are treated. Other concerns preclude a detailed discussion here, but other references (like J. P. Lowe, *Quantum Chemistry,* 2nd ed., Academic Press, Boston, 1993) can be consulted for details.

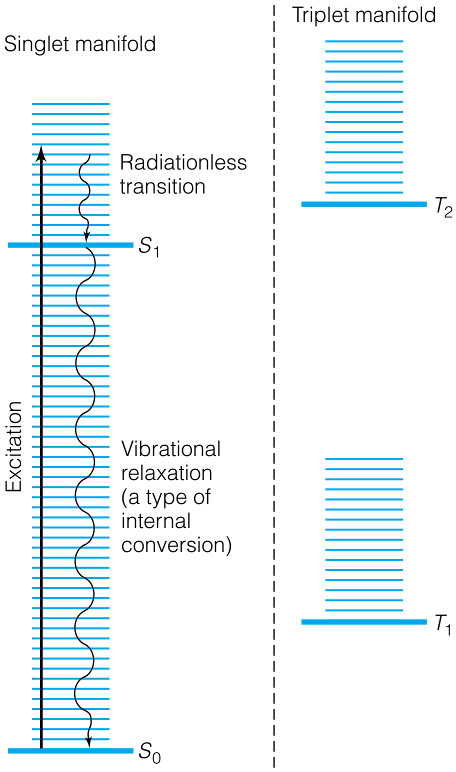

Figure 15.22 Many molecules have overlapping singlet (that is, $S = 0$, so $2S + 1 = 1$) and triplet ($S = 1$, so $2S + 1 = 3$) electronic states. Each of these electronic states has its own vibrational state manifold. In some cases, absorbed electronic energy is simply dissipated by being redistributed to the vibrations of the molecules, as shown. Normally, the singlet manifold of electronic states does not interact with the triplet manifold of electronic states via allowed electronic transitions. The numerical labels in the S and T states are used to differentiate one singlet (or triplet) state from another.

15.11 Fluorescence and Phosphorescence

In a perfect molecule, electronic transitions would go like this: absorption of a photon excites a molecule from initial (usually ground) state to excited state; excited state emits a photon having the same energy/frequency/wavelength and molecule goes from excited state to previous initial ground state. The first process, *excitation,* would be followed by the exact opposite process, called *de-excitation* or *decay.* Such processes would follow quantum-mechanical selection rules strictly.

In reality, electronic transitions stray somewhat from the ideal selection rules. In particular, when an excited electronic state decays to a lower electronic state, a photon having the same energy as the excitation photon might not be emitted. Instead, the molecule may de-excite by transferring the extra energy into various vibrational, rotational, or solid-state vibrational (called "phonon") modes of the sample. Ultimately, this excess energy is converted into heat energy. Such processes are called *radiationless transitions.*

There are other mechanisms for energy loss. The initial excited electronic state of a molecule is best thought of as a manifold of vibrational and rotational states superimposed on the electronic potential energy curve. (Such a view has been discussed previously.) In many cases, this manifold overlaps the energy range of another manifold of rotational and vibrational energies of a different electronic state (usually having lower electronic energy) that has the same spin multiplicity. This is an important requirement, because allowed transitions have the selection rule of $\Delta S = 0$. Such a system is illustrated in Figure 15.22. In some cases, the molecule will spontaneously change its state from the initial electronic state to the lower-energy electronic state of the *same multiplicity* without the emission of a photon. In doing so, any excess energy

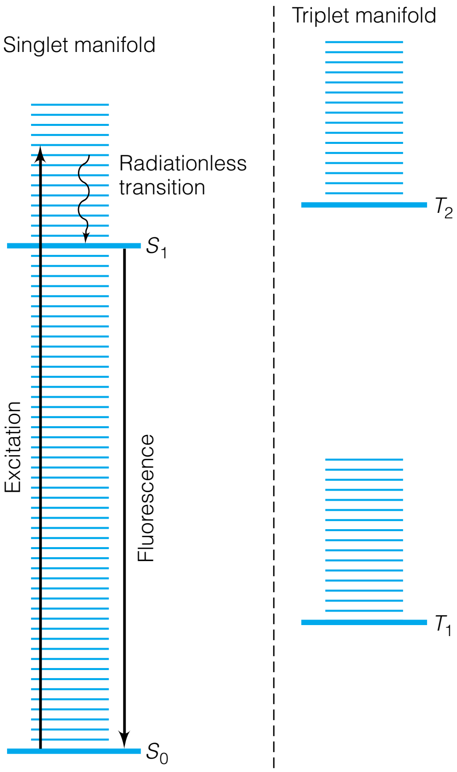

Figure 15.23 Fluorescence occurs when an atom or molecule absorbs a photon, vibrationally relaxes, and then emits a photon to go back to the ground state. The emitted photon is always lower in energy than the absorbed photon. Fluorescence is a relatively fast process.

is usually converted into vibrational energy. Such a process is called an *internal conversion,* because the electronic state changes within the molecule itself and does not include any other participant (like solvent, for example). Then, from this second electronic state, the molecule can emit a photon in a transition to the ground state. Because the second electronic excited state has lower electronic energy than the original electronic state, the photon emitted in the decay process has a lower energy than the photon absorbed in the excitation process. The exchange in excited states is usually very fast, on the order of 10^{-10} to 10^{-6} seconds. Emission of light of lower energy due to such internal conversions is called *fluorescence.* Figure 15.23 shows diagramatically the processes behind fluorescence.

Fluorescence spectra are useful because *two* excited electronic states are involved: one for the excitation process, and one for the decay process. A knowledge of *both* photons involved in the overall process is a better identification tool, and fluorescence spectroscopy is particularly useful in analytical chemistry. Since the excitation process must use a photon of higher energy than the decay process, ultraviolet excitation sources are particularly common in fluorescence spectroscopy. Many large molecules, which have complicated electronic states, can show fluorescence. Petroleum jelly, teeth, various minerals like zinc sulfide, and certain dyes fluoresce in the presence of higher-energy light. Fluorescent paints take advantage of this spectroscopic property. They absorb the relatively high-energy light and re-emit it as lower-energy photons, and in doing so appear brighter and, well, fluorescent. Fluorescent lightbulbs also take advantage of this property by using higher-energy photons emitted by mercury atoms and converting them into lower-energy visible light. Overall, the process is more energy-efficient than incandescent lightbulbs, which use red-hot filaments to generate light. (That is, incandescent lightbulbs are described by Planck's law whereas fluorescent light bulbs are described by quantum mechanics.)

Because fluorescence is a relatively fast process, it ends quickly when the source of excitation stops: again, on the order of 10^{-10} to 10^{-6} seconds. (Such time intervals are readily measurable with modern equipment, and the measurement of fluorescence processes is common in modern physical chemistry research.) However, the imposition of reality on molecular systems suggests that the $\Delta S = 0$ selection rule is not always followed, and in some cases a formally *forbidden* internal conversion occurs where $\Delta S \neq 0$. In most cases a singlet state ($2S + 1 = 1$) spontaneously transfers into a manifold defined by a triplet state ($2S + 1 = 3$). Such a conversion is illustrated by Figure 15.24. These conversions are called *intersystem crossings,* because electronic states of differing multiplicity are usually considered different electronic *systems* of the same molecule. After transferring to this new electronic state, the molecule emits a photon and transfers to a lower electronic state, just like in fluorescence. However, because intersystem crossings are formally forbidden by quantum mechanics, they usually take more time to occur. Timescales for photon emission for these processes are on the order of 10^{-4} to 10^{+4} seconds: much longer than fluorescence processes. This process is called *phosphorescence.* Phosphorescence is distinguished from fluorescence in two ways. First, the electronic states involved require a change in S (usually a forbidden process). Second, because of the timescale involved, phosphorescence continues even after the excitation source is turned off. (Strictly speaking, so does fluorescence, but the timescale implied here is one of human experience. Modern electronics can detect the decrease in fluorescence after the excitation source is removed,

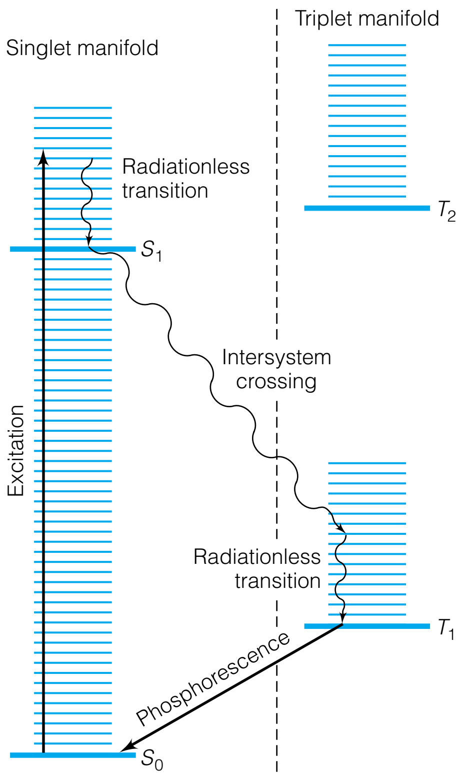

Figure 15.24 Phosphorescence occurs when there is a quantum-mechanically forbidden intersystem crossing (that is, when $\Delta S \neq 0$ occurs) and a state of different multiplicity is occupied. Because the transition from the triplet excited state to the singlet ground state is also formally forbidden, the transition from the T_1 state to the S_0 state takes a long time on the atomic or molecular timescale; phosphorescence is a relatively slow process.

but the timescale is much faster than the normal human perception. Phosphorescence, in terms of our own physical perception, is a much longer lasting phenomenon than fluorescence.)

Most glow-in-the-dark objects use the phosphorescence phenomenon because it is longer lasting. (Old watch dials with glow-in-the-dark watch faces actually relied on the fluorescence phenomenon, where a small amount of radium was mixed with zinc sulfide (a material that fluoresced) to provide a permanently glowing timepiece. Such radium-doped products are no longer made.) Glow-in-the-dark paint is made possible by a phosphorescence phenomenon, whereas Day-Glo or other so-called fluorescent paints take advantage of fluorescence.

15.12 Lasers

Lasers are a widespread and recognizable part of the modern technical society. They also represent such an unusual example of how electronic energy levels are utilized that a discussion of how (some) lasers work should be considered in this chapter. The very word "laser" is an example of how technology affects vocabulary. Originally an acronym for light amplification by stimulated emission of radiation, it has become a word in its own right. The maser (microwave . . .) preceded the laser, but it worked in the microwave region of the spectrum and was invisible to the eye and relatively low in energy. The fundamental theory behind lasers (and masers) was developed by Albert Einstein (Figure 15.25) around 1917.

In trying to understand the interactions between light and matter, Einstein defined three mechanisms. In order for an atomic or molecular system to go from a lower-energy state to an excited energy state, it must absorb a photon having a certain frequency (or wavelength or energy). Such absorption processes do not occur spontaneously, but must be stimulated by the presence of just the right photon. Einstein called this *stimulated absorption,* and noted that the rate of absorption must be proportional to the density of photons that have the right energy, labeled $\rho(\nu)$, and the concentration of atoms or molecules in the lower state, c_{lower}:

$$\text{rate} \propto \rho(\nu) \cdot c_{\text{lower}}$$

The photon density $\rho(\nu)$ can be determined from Planck's theory of light, assuming perfect blackbody behavior. Einstein introduced a proportionality constant B, now called the *Einstein coefficient of stimulated absorption*:

$$\text{rate of stimulated absorption} = B \cdot \rho(\nu) \cdot c_{\text{lower}} \qquad \textbf{(15.27)}$$

In addition, Einstein noted that a photon having the same energy can also induce, or *stimulate,* a transition in the opposite direction, from higher-energy state to lower-energy state. In doing so, the photon of just the right frequency causes a transition that emits another photon *having the same energy*. Einstein called this *stimulated emission,* and by the same arguments that led to equation 15.27 defined the *Einstein coefficient of stimulated emission, B′*:

$$\text{rate of stimulated emission} = B' \cdot \rho(\nu) \cdot c_{\text{higher}} \qquad \textbf{(15.28)}$$

where c_{higher} is the concentration of species in the excited state. Einstein was able to show that $B = B'$. Finally, he recognized another way a system can go from an excited state to a lower-energy state, a mechanism that excitations do not have: there could be a *spontaneous emission* of a photon of the right frequency. It is dependent on the concentration of species in the excited state but *independent* of the photon density $\rho(\nu)$. The rate of spontaneous emission is characterized by A, the *Einstein coefficient of spontaneous emission:*

$$\text{rate of spontaneous emission} = A \cdot c_{\text{higher}} \tag{15.29}$$

The total emission is the sum of the spontaneous and stimulated emission:

$$\begin{aligned}\text{rate of total emission} &= A \cdot c_{\text{higher}} + B \cdot \rho(\nu) \cdot c_{\text{higher}} \\ &= [A + \text{B} \cdot \rho(\nu)]c_{\text{higher}}\end{aligned} \tag{15.30}$$

Under normal circumstances, the rate of emission is always greater than the rate of absorption, so that most atomic and molecular systems are in their lowest-energy states. The three interactions are illustrated in Figure 15.26.

By thinking of the electronic transition as a "vibration" of an electron, Einstein derived the mathematical forms of the coefficients A and B as

$$A = \frac{8\pi^2 e^2 \nu^2}{(4\pi\epsilon_0)m_e c^3} \tag{15.31}$$

$$B = \frac{\pi e^2}{(4\pi\epsilon_0)hm_e\nu} \tag{15.32}$$

where e is the charge on the electron in coulombs, ν is the frequency of the transition in s^{-1}, m_e is the mass of the electron in kg, h is Planck's constant, and c is the speed of light in m/s. The constant ϵ_0 is necessary to relate the units of charge, coulombs, to SI units. The *ratio A/B* is

$$\frac{A}{B} = \frac{8\pi h\nu^3}{c^3} \tag{15.33}$$

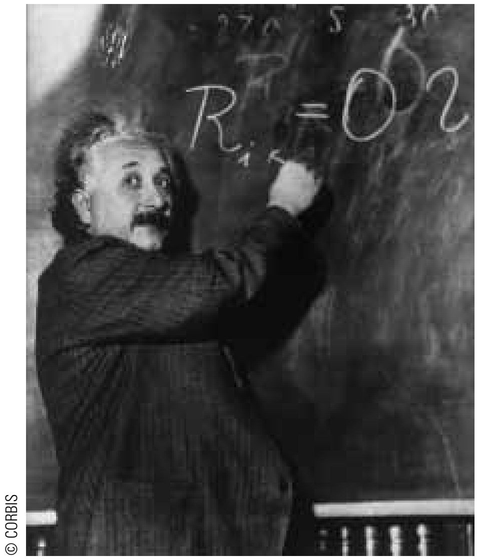
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Figure 15.25 Albert Einstein laid down the basic theory of lasers in 1917, over 40 years before they were developed.

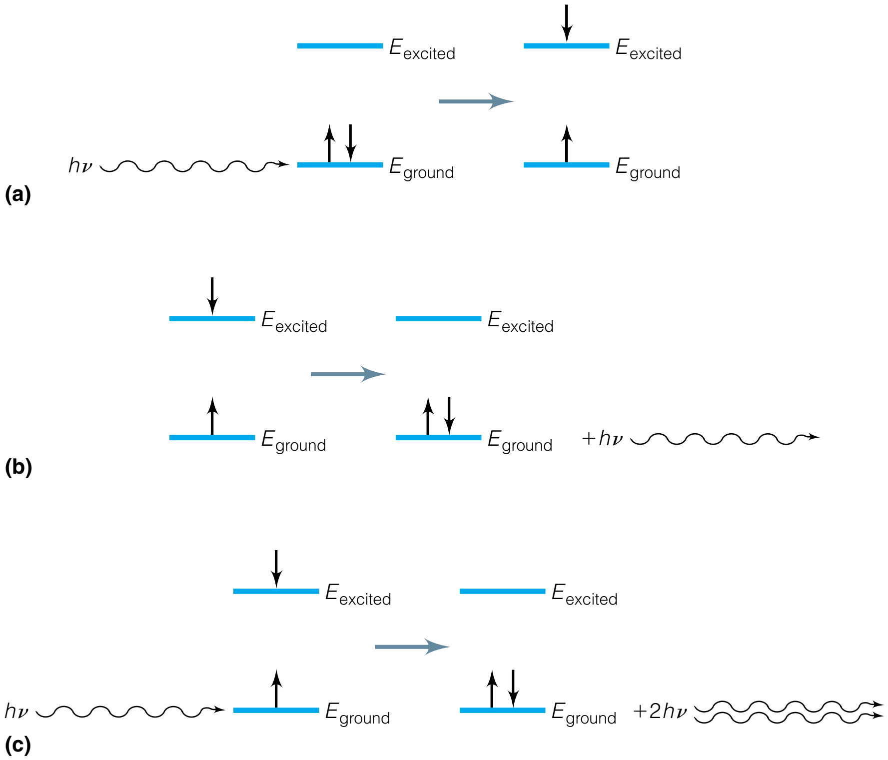

Figure 15.26 (a) Stimulated absorption, which defines Einstein's coefficient B. (b) Spontaneous emission, which defines Einstein's coefficient A. (c) Stimulated emission, which defines Einstein's coefficient B'. In stimulated emission, the two photons have the same wavelength and phase, as indicated.

and the only varying factor in this ratio is ν, the frequency of the transition. What this ratio says is that the greater the frequency of the transition, the larger the chance that spontaneous emission, determined by A, will occur over stimulated emission, which is measured by B.

Example 15.14

Lasers make use of stimulated emission. Using equation 15.33, suggest a reason why red lasers are easy to engineer but blue lasers are more difficult.

Solution

The ratio in equation 15.33 has the third power of the frequency, ν, in the numerator. Therefore, the higher the frequency, the higher the ratio of spontaneous emission to stimulated emission. An electronic transition that occurs in the blue region of the spectrum, which has roughly twice (2×) the frequency of the red region of the spectrum, has a $(2)^3 = 8$ times greater chance of decaying by spontaneous emission than by stimulated emission. If lasers depend on stimulated emission, blue lasers are therefore correspondingly more difficult to produce.

Example 15.15

Determine the ratio of spontaneous to stimulated emission for a transition that occurs at the following wavelengths.

a. $\lambda = 21.0$ cm, a wavelength that has implications in astronomy

b. $\lambda = 300.0$ nm, which is in the middle UVB part of the spectrum.

c. Comment on the difference in the two ratios.

Solution

a. The frequency in s^{-1} must be determined first:

$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^{8}\ \text{m/s}}{21.0\ \text{cm}} \times \frac{100\ \text{cm}}{1\ \text{m}} = 1.428 \times 10^{9}\ \text{s}^{-1}$$

Substituting into the formula for the ratio A/B:

$$\frac{A}{B} = \frac{8\pi h\nu^3}{c^3} = \frac{8\pi(6.626 \times 10^{-34}\ \text{J·s})(1.428 \times 10^{9}\ \text{s}^{-1})^3}{(2.9979 \times 10^{8}\ \text{m/s})^3}$$

$$= 1.800 \times 10^{-30}\ \text{kg/(m·s)}$$

This is a very small ratio (whose units are a consequence of equation 15.33).

b. Again, we determine frequency:

$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^{8}\ \text{m/s}}{300.0\ \text{nm}} \times \frac{10^{9}\ \text{nm}}{\text{m}} = 9.993 \times 10^{14}\ \text{s}^{-1}$$

and substitute it into the formula for A/B:

$$\frac{A}{B} = \frac{8\pi h\nu^3}{c^3} = \frac{8\pi(6.626 \times 10^{-34}\ \text{J·s})(9.993 \times 10^{14}\ \text{s}^{-1})^3}{(2.9979 \times 10^{8}\ \text{m/s})^3}$$

$$= 6.168 \times 10^{-13}\ \text{kg/(m·s)}$$

c. Although still a small number, the second result is 17 orders of magnitude larger than the first answer. This means that spontaneous emission is almost a billion billion times more likely for light having wavelength of 300.0 nm than a wavelength of 21.0 cm.

Before we get to lasers themselves, we need to jump ahead a little (to Chapters 17 and 18). The basic idea is that thermal energy may be sufficient to cause excited quantum states to be populated to a significant degree—depending on the amount of thermal energy available and the amount of energy necessary to reach the excited state. It will be shown later that if an energy level is ΔE energy units (typically, joules) above the ground state, then the *fraction of the total species,* labeled F, that is in the excited state is given by the equation

$$F = e^{-\Delta E/kT} \tag{15.34}$$

where T is the absolute temperature and k is Boltzmann's constant. We are assuming that the two energy states involved are nondegenerate. Otherwise, degeneracy must be included (see Chapters 17 and 18). If the molar energy were used, then the equation would be

$$F = e^{-\Delta E/RT}$$

where R is the ideal gas law constant. For example, rotational levels in gas-phase molecules can be thermally excited, so that the most populated rotational eigenstate is not the $J = 0$ state (see Chapter 14). Vibrational energy states are often thermally populated. Electronic energy levels are rarely thermally populated because most ambient temperatures are so low relative to the amount of excitation energy that practically all systems are in the ground electronic state. Systems whose atoms or molecules follow equation 15.34 are said to be at *thermal equilibrium.* Each possible energy level has a certain fraction of molecules having that energy level. The energy levels are said to have a certain *population* of systems inhabiting that energy. A system at thermal equilibrium is illustrated in Figure 15.27.

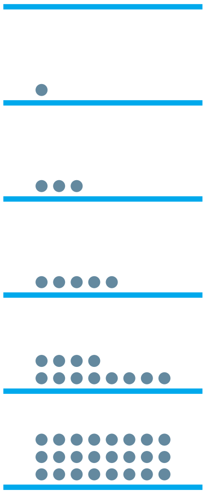

Figure 15.27 Thermal equilibrium is characterized by this type of population of excited states that might be accessed by thermal energy alone. The higher the energy level, the smaller the population. Statistical analysis indicates that the decrease in population of the energy levels is exponential in nature.

Now, to lasers. Because there is both spontaneous and stimulated emission, systems in thermal equilibria usually have more molecules in a lower-energy electronic state than in a higher-energy electronic state. Suppose, however, that a certain electronic state decays rather slowly. We call this a *long-lived* or *metastable excited state.* Suppose too that we can excite the atoms or molecules into the metastable excited state faster than that excited state decays. Under those circumstances, we can populate the excited state over and above the fraction dictated by thermal equilibrium, which is given by equation 15.34. Such a situation is called a *population inversion* and is illustrated in Figure 15.28. Population inversions can be achieved by light excitation, by electrical discharge, or even by chemical reaction. Typically, at least three energy levels are needed to establish a population inversion. There is the lowest-energy initial state (sometimes but not always the ground state), and an initial excited state that decays rather quickly into a second, lower-energy, long-lived excited state. It is between the lower-energy excited state and the ground state that the population inversion is established.

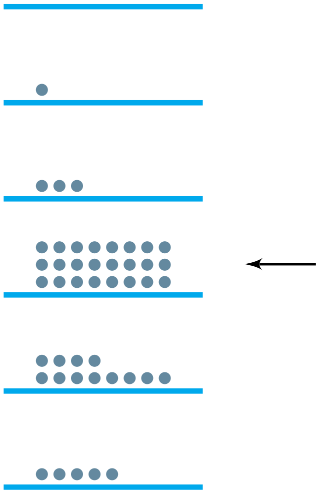

Figure 15.28 A population inversion is achieved when higher energy levels are more populated than is predicted by a thermal equilibrium (see Figure 15.27). Here, the third energy level is experiencing a population inversion. Population inversions are not normally encountered, but can be easily engineered. All lasers require a population inversion as part of the laser process.

Even when a population inversion is established and maintained, both spontaneous and stimulated emission still occur. However, the stimulated emission is the key. A photon of a particular wavelength stimulates the emission of another photon of the same wavelength, which can stimulate the emission of a photon of the same wavelength, which can stimulate the emission of a photon of the same wavelength, which can . . . and so the building up of a collection

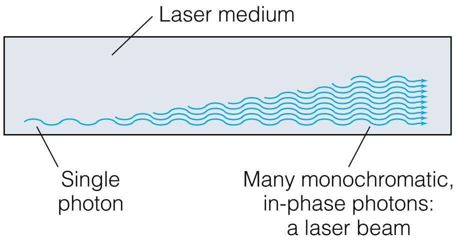

Figure 15.29 When a population inversion is established, stimulated emissions can build until the number of photons is extremely high, yielding a very bright light. This is called light amplification by stimulated emission of radiation, or *laser*.

of photons, all having the same wavelength (and phase, as it turns out), occurs. Because all of these photons have the same wavelength, the collection of photons is called *monochromatic* ("same color"). (The individual photons usually have the same phase and specific polarization properties, too, but we will omit discussion of these properties. They are, however, important for various applications of lasers.) This process is shown in Figure 15.29. It is called "light amplification by stimulated emission of radiation," which produced the acronym LASER and later entered the language as *laser*. The very first laser was built by the American physicist Theodore Maiman in 1960 using a ruby rod, but the concept of stimulated emission was first demonstrated by the Columbia University physicist Charles Townes in 1953. Using ammonia, he and his students constructed a device that amplified microwave radiation using a similar stimulated-emission principle ("microwave amplification . . . ," leading to the term "maser"). Realizing a similar process for visible light, Townes and Arthur Schawlow published such ideas in 1958, and in 1964 Townes shared a Nobel Prize with the Soviet scientists Alexander Prokhorov and Nikolai Basov, who developed the theory of lasers independently.

A simplified diagram of a laser is shown in Figure 15.30. Although the population inversion is the key to producing laser action ("lasing"), the engineering of the laser is also crucial. In most cases, the active material is tubular with each of the transverse ends of the material meeting a mirror. These two mirrors are important because they make the photons travel back and forth through the laser medium, thereby increasing the chances that they will induce stimulated emission. Even if one of the mirrors reflects 100% of the photons and the other reflects only 95–99% of the light (the leftover 1–5% is transmitted), the transmitted light makes a monochromatic beam of very high intensity. This emitted *laser beam* is a rich source of photons of a particular energy.

A more complete discussion of lasers is beyond our scope. On the other hand, it is worth discussing a few points using specific lasers as examples. The very first laser was built around a ruby rod (Figure 15.31). Ruby is crystalline sapphire, aluminum oxide, Al_2O_3, that has been doped with a few hundredths of a percent of Cr^{3+} ions. A partial electronic energy diagram of Cr^{3+} is given in Figure 15.32. The ground state of Cr^{3+} is $^4A_2$. Pulses of visible light are used to excite electrons into either an excited $^4T_2$ or $^4T_1$ state. (These term symbols are actually irreducible representations combined with multiplicities.) Within 10^{-7} s, there is a *nonradiative transition* into an E electronic excited state. Since this transition occurs very quickly, a population inversion is established in

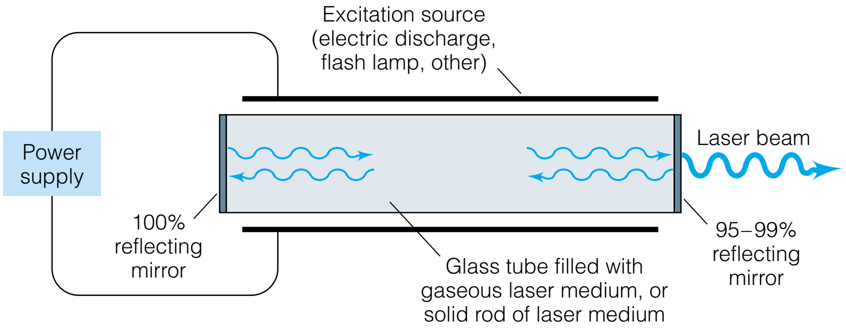

Figure 15.30 Simple diagram of a laser. Photons bounce back and forth inside the lasing medium, reflected off mirrors on each end, stimulating the production of photons of the same wavelength and phase. One of the mirrors lets some of the photons out.

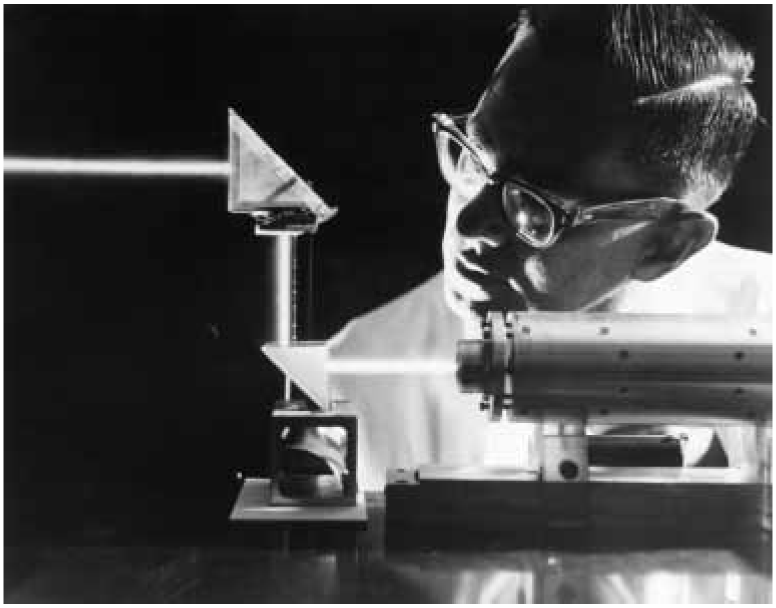
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Figure 15.31 A ruby laser in operation.

short order and a pulse of lasing action occurs at a wavelength of 694.3 nm, which is in the red region of the spectrum. Typically, ruby crystals are a few millimeters wide and several centimeters long, and are still used today in some lasers. Because three individual electronic states contribute to the laser action, the ruby laser is an example of a *three-level laser system.* If the electronic excitation is caused by a pulse of light, the resultant laser action is also a pulse of laser light. This is an example of a *pulsed laser.* It can also be operated continuously using constant illumination by an excitation source. In such a configuration, the ruby laser is an example of a *continuous-wave* (or cw) laser.

Direct electrical excitation using an electrical discharge is used to excite atoms in the helium-neon or He-Ne (actually pronounced "hee-nee") laser. An

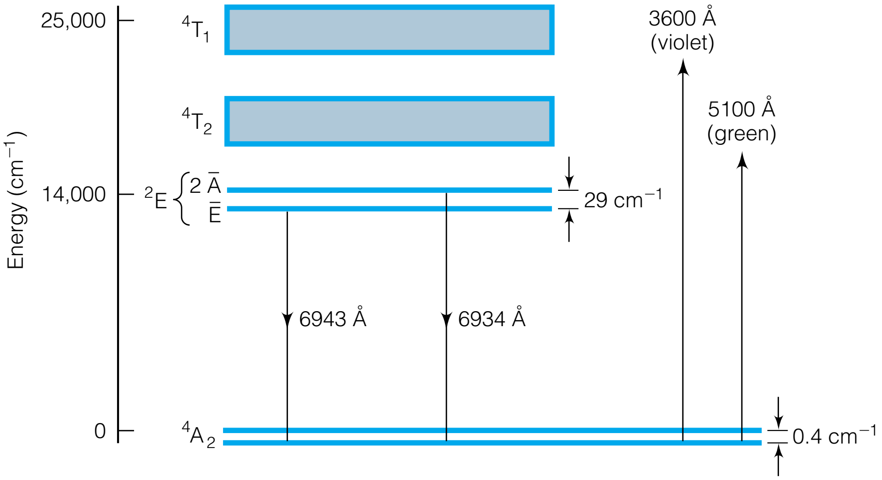

Figure 15.32 Energy levels of the Cr^{3+} ion involved in the ruby laser, the first laser to be developed. The ions are excited by green or violet light, a population inversion is established, and red laser light is produced by stimulated emission. *Source:* Reprinted with the permission of Simon & Schuster from *The Laser Book* by Clifford Laurence. Copyright © 1986 by Clifford L. Laurence.

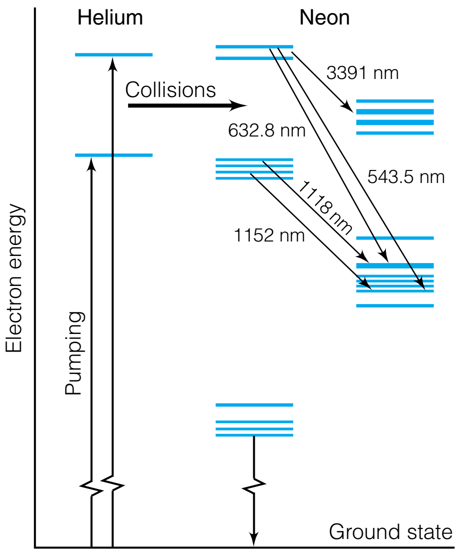

Figure 15.33 Energy levels of the He-Ne laser, one of the most prevalent lasers in society (witness grocery store scanners). Helium atoms are initially excited, but they transfer energy very effectively to neon atoms, which participate directly in the lasing process. Note that several possible transitions are possible for laser action, each one having a different color. Most common is the 632.8-Å laser, which is bright red. *Source:* From M. J. Beesley, *Lasers and Their Applications.* © Taylor & Francis, 1971. Reprinted with permission from the publisher.

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Figure 15.34 A He-Ne laser in operation.

energy level diagram for this laser is shown in Figure 15.33, with Figure 15.34 showing an example of a He-Ne laser in operation. The He-Ne laser is an example of an *ion laser,* since He^+ and Ne^+ ions are the important electronic systems. Figure 15.33 shows that two of the excited electronic states of He^+ are almost coincident with excited electronic states of Ne^+, thereby increasing the ability to transfer electrons to Ne^+ excited states and produce a population inversion. The He-Ne system is an example of an electronic system that has several possible lower-energy states that can participate in the lasing process, producing different wavelengths of laser light. How does one select which state produces the laser beam? For the He-Ne system, one can modify the reflectivity of the mirrors so that only one wavelength of light is effectively reflected back and forth through the laser medium, stimulating more photons of the exact same wavelength. In this way, the transition occurring at 632.8 nm, in the red part of the spectrum, is preferred and is the dominant color of He-Ne lasers. (Green He-Ne lasers are also available, which lase at 543 nm.) The other transitions, at 3.39 μm and 1.15 μm, occur in the infrared portion of the spectrum but are largely unused. The 1.15-μm laser beam is historically important because it was the wavelength of the first laser made from a gaseous laser medium.

Because four energy levels are involved in the laser action of He-Ne lasers (consult Figure 15.33), they are referred to as *four-level laser systems.* He-Ne lasers are perhaps the most common lasers in use, among other things for surveying and for scanning prices in a grocery store. Although not considered high-energy lasers, they are a very bright light and can cause eye damage if one looks into the laser beam.

An electrical discharge using the Ar^+ ion also produces laser action at multiple wavelengths. These lasers are among the more common higher-energy lasers, producing laser light in the green ($\lambda = 514.6$ nm) and blue ($\lambda = 488.8$ nm) region of the spectrum. *Tuning* of the laser light frequency is done by changing the resonance characteristics of the lasing chamber. For example, a prism can be used to direct one wavelength of light toward a mirror for stimulated emission, and (because the index of refraction is different for different wavelengths of light) to direct other wavelengths in a slightly different direction to avoid reinforcing them through stimulated emission.

The carbon dioxide laser uses a population inversion based on the rovibrational energy levels of the CO_2 molecule (and so technically is not welcome in a discussion of electronic energy levels). The energy level diagram is shown in Figure 15.35. The CO_2 laser is infamous because it does what lasers are expected to do in science fiction: blast holes in objects. The wavelength of CO_2 lasers is 10.6 μm, which is in the infrared portion of the spectrum. Many solid objects absorb infrared light very well, and since CO_2 laser light is a very potent source of infrared photons, it has the capability of heating up things very quickly. This is coupled with the ~25% efficiency of conversion of the excitation energy into light energy, an efficiency almost unmatched by any other popular laser medium.

15.13 Summary

Transitions among electronic energy levels are among the most crucial processes that occur in all of chemistry. For atomic systems, they are fairly well understood. At the very least, there is an established convention for labeling the electronic energy levels and a rather rigorous understanding of the allowed and

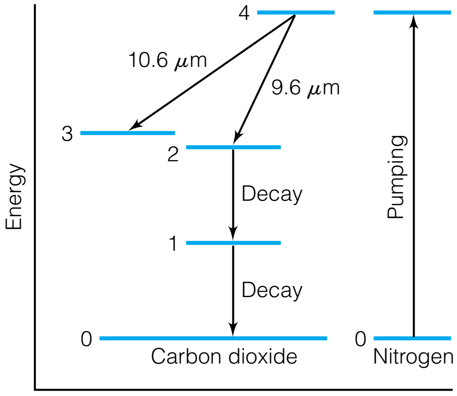


Figure 15.35 Energy levels of the CO_2 laser. Lasing at 10.6 μm, which is in the IR region of the spectrum, means that a CO_2 laser can heat objects very quickly. CO_2 lasers are actually used for cutting and welding. *Source:* From M. J. Beesley, *Lasers and Their Applications.* © Taylor & Francis. Reprinted with permission from the publisher.

forbidden transitions. For molecules, there is a convention based on the character table for the symmetry point group, but wide-ranging generalities are difficult (except perhaps for conjugated π electron systems, as described by the Hückel theory). Most in-depth discussion of electronic transitions of molecules is best confined to a specific discussion of that molecule instead of a general discussion of electronic spectroscopy (unlike rotational and vibrational spectroscopy, which can be well developed without defining the molecular system). Transitions among electronic energy levels produce laser beams (as we know thanks to Einstein's analysis of electronic transitions), but laser action is not limited to electronic energy level transitions. In the visible region of the spectrum, however, a laser represents a superb modern example of how we have been able to understand and utilize transitions between the electronic energy levels of atoms and molecules.

EXERCISES FOR CHAPTER 15

15.2 Selection Rules

15.1. Linearly polarized light can be assigned a specific irreducible representation of a symmetry point group. If the electronic ground state of benzene has A_{1g} symmetry and y-polarized light has the label E_{1u}, what are the symmetry label(s) of allowed excited electronic states? Use the D_{6h} character table in Appendix 3.

15.2. Explain in your own words why electronic transitions are considered dipole-moment allowed.

15.3 The Hydrogen Atom

15.3. Determine the value of R for deuterium (^{2}H) and tritium (^{3}H) using equation 15.3. You will have to look up the masses of the D and T nuclei. By what percentage do these R values differ from that for hydrogen?

15.4. Harold Urey discovered deuterium in 1931 by very carefully evaporating four liters of liquid hydrogen down to a single milliliter and measuring the electronic spectrum. New lines in the atomic spectrum confirmed the presence of "heavy hydrogen" right where quantum theory predicted. Calculate the expected positions of the four visible lines of the Balmer series for deuterium atoms. (See Chapter 9 for the details on the Balmer series for H atoms.)

15.5. Draw a Grotrian-type diagram for the first four lines of the Lyman series in the hydrogen atom spectrum. Be sure to include all allowed transitions.

15.6. What is the value of the change in energy, ΔE, for the (n, ℓ) transition of the hydrogen atom labeled $(3, 2) \rightarrow (3, 1)$? Justify your answer.

15.4 Orbital and Spin Angular Momenta

15.7. List the possible values of L, M_L, S, M_S, J, and M_J for the following: **(a)** two coupled p electrons, **(b)** two coupled f electrons, **(c)** two coupled electrons, one a p electron and one a d electron. Remember that the z-component quantum numbers depend on the values of the total angular momentum quantum numbers.

15.8. A proton also has spin of $\frac{1}{2}$. What are the possible values of M_S for a hydrogen nucleus? A deuterium nucleus has a nuclear spin (labeled with the letter I) of 1. Does it have the same values of M_S?

15.9. Low-energy electronic spectra of Al atoms, under high resolution, appear as multiplets. Suggest a reason for this.

15.10. What are the possible *observable values* of orbital and spin angular momenta and their z components for **(a)** a single d electron, **(b)** a single f electron, **(c)** a single g electron? What are the possible values of j and m_j for each case?

15.11. The sodium D lines appear at 5890 and 5896 Å. Using this information, what is the difference in energy between the $j = \frac{1}{2}$ and $j = \frac{3}{2}$ states in sodium?

15.5 Term Symbols; Russell-Saunders Coupling

15.12. What is the term symbol for the ground state of **(a)** Li, **(b)** Al, **(c)** Sc?

15.13. Show that the maximum multiplicity term symbols for half-filled subshells will always have an S (that is, $L = 0$) term symbol. Do this by considering that L can also be determined from the sum of the values for the m_ℓ quantum numbers of the electrons in the hydrogen-like orbitals.

15.14. In some tables where the excited states within the $1s^2\ 2s^2\ 2p^2$ electron configuration of C are labeled with their energy values, the $^3P_0$ state is not labeled with an energy. Why?

15.15. Determine the term symbols and which is the ground-state term symbol for a hypothetical element having an h^2 electron subshell configuration for its ground state.

15.16. List all of the possible term symbols of allowed excited states of the atom that has a ground state of $^3D_1$.

15.17. Many times, electronic spectra are measured when the sample is very cold so that all of the electrons are in the ground electronic state. For samples that have low-lying excited states, liquid helium can be used. Ni is one example, having an excited electronic state at ~200 cm^{-1}. If the Ni atom has a term symbol of $^3F_2$ for its electronic ground state, what will be the allowed excited states?

15.18. The Co^{2+} ion has a d^7 electron configuration and a ground-state term symbol of $^4F_{9/2}$. List the possible term symbols for excited states that will participate in allowed transitions.

15.6 Diatomic Molecules

15.19. Why is the total angular momentum of a diatomic molecule, labeled $\mathbf{J}$, quantized?

15.20. Why do heteronuclear diatomic molecules not use the labels g and u on their term symbols?

15.21. Use group-theoretical arguments to determine the term symbols for Li_2, which has two unpaired electrons in doubly degenerate π_u molecular orbitals.

15.22. In some cases where diatomic oxygen is a product of a chemical reaction, O_2 is formed where both electrons are paired in the same Π_g molecular orbital and so are in a $^1\Sigma$ electronic excited state. The decay of this state to the ground state occurs slowly. Suggest why the decay is so slow.

15.23. Determine the ground-state term symbol of the acetylide ion, $C_2{}^{2-}$. Use the molecular orbital diagram for oxygen for assistance.

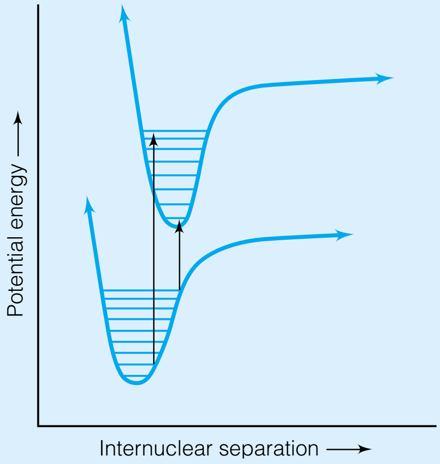


Figure 15.36 Two vibronic levels of a molecule.

15.7 & 15.8 Franck-Condon Principle and Polyatomic Molecules

15.24. Figure 15.36 shows two vibronic levels of a molecule. Indicate which sets of energy levels should have the largest Franck-Condon overlap integral. Explain your answer.

15.25. Indicate, on the basis of general principles, whether or not the following polyatomic ions are colored. **(a)** Nitrate, NO_3^- **(b)** Permanganate, MnO_4^- **(c)** Ammonium, NH_4^+ **(d)** Dichromate, $Cr_2O_7^{2-}$ **(e)** Peroxide, O_2^{2-} **(f)** Acetylide, C_2^{2-}

15.26. For an electronic spectrum that has both vibrational *and* rotational structure (a rovibronic spectrum), suggest a form for the complete transition moment.

15.27. Determine the symmetry labels of the allowed excited states of H_2O if the ground electronic state has a symmetry label of $^1A_1$. (H_2O has C_{2v} symmetry.)

15.9 & 15.10 Hückel Approximations and Aromaticity

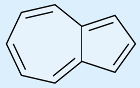
15.28. Justify in words why $S_{11} = S_{22} = S_{33} = S_{44}$ in the Hückel approximation of the π orbitals of butadiene.

15.29. What would change in the Hückel approximation of ethylene if deuterium atoms were substituted for the hydrogen atoms in the molecule? Explain your reasoning.

15.30. Construct the Hückel determinants for cyclobutadiene and cyclopentadiene. In what ways are they alike? In what ways are they different?

15.31. Explain why cyclopentadiene easily accepts an electron to become cyclopentadienide ($C_5H_5^-$, which is abbreviated Cp in organic or organometallic chemistry).

15.32. Consider the following molecule:



Azulene

Why can its stability be attributed to an internal charge separation with a + charge in the seven-membered ring and a − charge in the five-membered ring?

15.33. Within each of the following groups, predict which cyclopolyenes will be aromatic: **(a)** neutral, **(b)** single negative charge, and **(c)** double negative charge.

15.34. Do the same as in exercise 15.33, but for cyclopolyenes with **(a)** a single positive charge and **(b)** double positive charge.

15.11 & 15.12 Fluorescence, Phosphorescence, and Lasers

15.35. Why can a population inversion *not* be achieved by simply heating a potentially laser-active material?

15.36. Suggest why phosphorescence spectra are sometimes better for identifying useful electronic transitions for possible laser transitions than are fluorescence spectra.

15.37. Would the light from fireflies be considered an example of a fluorescence or a phosphorescence process?

15.38. Why is it not possible to obtain blue fluorescence from a transition that initially absorbs red light?

15.39. CO_2 lasers are among the most powerful cw lasers available; their most commonly emitted wavelength is 10.6 μm. How many 10.6-μm photons are generated each second from a CO_2 laser that emits 300,000 J per second? (That makes it a 300-kilowatt laser.)

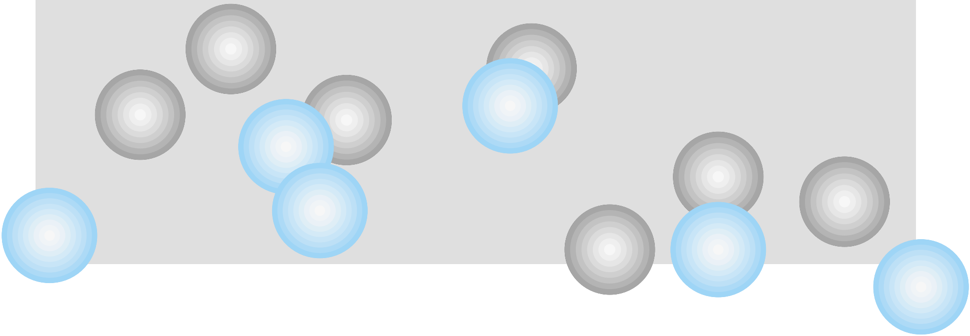
15.40. How many 632.8-nm photons must a He-Ne laser emit per second to achieve a power of 1 J/s?

15.41. Many high-power lasers emit only a little bit of energy but in an extremely short pulse. What is the power of a laser that emits a 300-millijoule pulse in 2.50 nanoseconds?

15.42. Explain why X-ray lasers would be extremely difficult to build.

16

Introduction to Magnetic Spectroscopy



WE HAVE MADE PASSING MENTION of the effects of magnetic fields on atomic or molecular energy levels. For example, we have stated several times that magnetic fields remove the degeneracies of the various m_ℓ levels within a single ℓ value. However, we have not really considered the idea of magnetic spectroscopy. We have alluded to the fact that magnetic fields can change the energies of electrons having different m_ℓ quantum numbers. You may also be aware of the medical imaging technique called magnetic resonance imaging (MRI), which is an important application of magnetic spectroscopy.

The very term "magnetic spectroscopy" is a bit of a misnomer. Although electricity and magnetism are elements of the same phenomenon (hence the word *electromagnetism*), we typically experience electricity as an ability to do electrical work and magnetism as a sort of static field. Perhaps in an experiential sense, this is accurate. But magnetic fields do affect quantum states at the atomic and molecular level, and so have an effect in spectroscopy. In *magnetic spectroscopy,* a magnetic field is imposed on a sample while it is probed with electromagnetic radiation. Although the presence of a magnetic field might not seem to make a lot of difference, we can get a lot more information about the quantum states of an atom or molecule when we use a magnetic field along with light. In this chapter, we will consider a few examples of magnetic spectroscopy.

16.1 Synopsis

Initially, we will look at magnetic fields and magnetic dipoles and see how they interact. Even though most of the magnetic spectroscopies we will discuss are based on quantum mechanics, an understanding of magnetic fields and dipoles from classical mechanics will be useful. When we get to magnetic spectroscopies, we will first consider the Zeeman effect: a splitting of the electronic energy levels of an atomic system by a magnetic field. Observation of the Zeeman effect went almost hand in hand with the development of quantum mechanics and provided some useful and necessary experimental evidence for the existence of the various quantum numbers. The Zeeman effect is a relatively straightforward and useful type of magnetic spectroscopy. More involved and more intricate are the various types of magnetic resonance (or MR) spectroscopy. In MR spectroscopy, an experimenter has the opportunity to vary both the electromagnetic radiation and the magnetic field strength until the difference between the split energy levels equals the energy of the photon and so a photon is absorbed: that is, a resonance is established. The two major forms of MR spectroscopy are nuclear magnetic resonance and electron spin resonance (also called electron paramagnetic resonance, depending on the type of atomic or molecular system). As their names suggest, one deals with magnetic field interactions with the nucleus and the other deals with magnetic field interactions with the electrons. Different and useful information can be obtained with both.

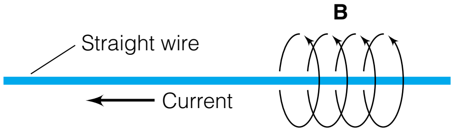


Figure 16.1 Current traveling through a straight wire causes the formation of a cylindrical magnetic field, labeled **B**.

16.2 Magnetic Fields, Magnetic Dipoles, and Electric Charges

Classically, *magnetic fields* (more formally called "magnetic inductions") are caused by moving charges. If a current I were flowing through a wire in one direction, then the magnetic field is a circular vector mapping out a cylinder around the wire and having its center at the wire, as in Figure 16.1. The magnetic field strength depends on the distance, labeled r, from the wire. The magnitude of the magnetic field strength vector, labeled **B**, is given by the equation

$$B = |\mathbf{B}| = \frac{\mu_0 I}{2\pi r} \tag{16.1}$$

where the | | symbols are used to indicate the magnitude of a vector and μ_0 is a physical constant called the *permeability of a vacuum.* Its value is $4\pi \times 10^{-7}$ tesla·meter/ampere, or T·m/amp. The *tesla* is one unit of magnetic field strength, and is named after the erratic scientific genius Nikola Tesla (Figure 16.2). In terms of basic units, a tesla is equal to a kg/(coulomb·s). There is another unit of magnetic field strength, the *gauss,* abbreviated G, which is equal to 10^{-4} T.

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Figure 16.2 Nikola Tesla (1856–1943) was born in Croatia and emigrated to the United States in 1884. Although he ultimately turned into a rather eccentric character, his work in electricity and magnetism almost earned him the 1912 Nobel Prize. He helped pioneer the use of alternating current (AC) over direct current (DC) in the fledgling electrical power industry.

The direction of the magnetic field vector is given by the "right-hand rule": if you point your right hand's thumb in the direction of the current, the right hand's fingers would curl in the direction of the magnetic field. This is illustrated in Figure 16.3.

Conversely, consider an electrical current I that is going around in a circle, a closed loop, as in Figure 16.4. This loop has some area, labeled A. According to the classical theory of electromagnetism, this loop of current induces a linear magnetic effect called a *magnetic dipole.* It is called a dipole because it is a vector that has a specific direction, which is normally considered the "positive" or "north" pole of the dipole (the direction the vector is *from* is considered the "negative" or "south" pole). For the magnetic dipole vector, labeled $\boldsymbol{\mu}$, the magnitude is

$$\mu = |\boldsymbol{\mu}| = I \cdot A \tag{16.2}$$

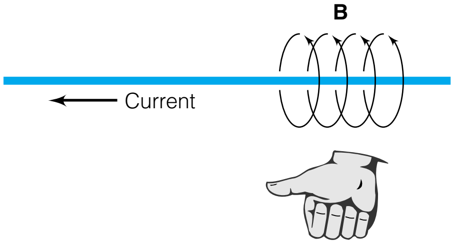

Figure 16.3 The right-hand rule is used to determine the direction of the magnetic field vectors. If the thumb of the right hand is pointed in the direction of the current, the fingers curl in the direction of the magnetic field, as shown.

The unit of the magnetic dipole is ampere·meter^2. The direction of the magnetic dipole vector is also given by the right-hand rule. If you curl your fingers around the closed loop in the direction of the current, your thumb points in the direction of the magnetic dipole vector (that is, toward the north pole end). The magnetic dipole vector and the right-hand rule are illustrated in Figure 16.4. At this point, you should be able to differentiate between a magnetic field and a magnetic dipole. They are two different things.

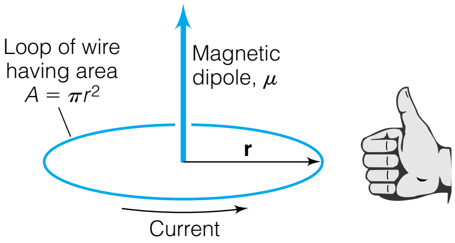

Figure 16.4 Current in a loop causes the formation of a magnetic dipole, which is different from a magnetic field. However, the right-hand rule is also used to determine the direction of the magnetic dipole, as shown.

Currents consist of individual electrical charges, usually electrons. We can therefore consider the magnetic fields produced by a single electron as it moves—at least classically.

Example 16.1

For a distance of 1 m from a single straight wire, calculate the magnetic field produced by each of the following:

a. A single electron passing by a point each second

b. A mole of electrons passing by a point each second

Solution

a. At 1.602×10^{-19} coulombs per electron, the current I in this case is 1.602×10^{-19} C/s, or 1.602×10^{-19} amp. Substituting into equation 16.1, one gets

$$B = \frac{(4\pi \times 10^{-7}\ \mathrm{T{\cdot}m/amp})(1.602 \times 10^{-19}\ \mathrm{amp})}{2\pi(1\ \mathrm{m})} = 3.204 \times 10^{-26}\ \mathrm{T}$$

b. One mole of electrons has a charge of approximately 96,500 C (this is Faraday's constant) for a current of 96,500 amps. (In reality, such a current would probably destroy the wire.) Substituting this value into equation 16.1:

$$B = \frac{(4\pi \times 10^{-7}\ \mathrm{T{\cdot}m/amp})(96{,}500\ \mathrm{amp})}{2\pi(1\ \mathrm{m})} = 0.0193\ \mathrm{T}$$

Compare the answer from part b to the value for Earth's natural magnetic field, which is approximately 0.6 gauss, or 6×10^{-5} T. Common currents around the home, office, or lab are 15 to 30 amperes, so the magnetic fields to which one might be exposed from normal electrical wiring are on the order of magnitude of Earth's own magnetic field.

Example 16.2

Calculate the magnetic dipole magnitude of the following:

a. 1 ampere of charge in a superconducting ring having a radius of 0.500 m

b. A current of 6.58×10^{15} amperes moving about a ring having a radius of 0.529Å. (This is equivalent to an electron in the first Bohr radius of the Bohr hydrogen atom.)

Solution

a. The area of the circle is $\pi r^2 = (3.14159)(0.5\ \mathrm{m})^2 = 0.785\ \mathrm{m}^2$. Therefore, the magnetic dipole for 1 ampere at 0.5 m radius is $0.785\ \mathrm{amp{\cdot}m^2}$.

b. The area of this smaller ring is $(0.529 \times 10^{-10}\ \mathrm{m})^2 = 2.80 \times 10^{-21}\ \mathrm{m}^2$. The magnetic dipole in this case is simply $(6.58 \times 10^{15}\ \mathrm{amp}) \times (2.80 \times 10^{-21}\ \mathrm{m}^2) = 1.84 \times 10^{-5}\ \mathrm{amp{\cdot}m^2}$. [Although this is a smaller magnetic dipole than that in part a, it is due to a single (classical) electron.]

Magnetic effects like fields and dipoles interact with each other. It's like two bar magnets interacting, either both north or south poles interacting to repel each other, or a north and a south pole of a magnet attracting each other. A potential energy defines their interaction (a repulsive potential energy or an attractive potential energy, respectively: see Figure 16.5). It is the same with a magnetic field and a magnetic dipole. When a magnetic dipole $\boldsymbol{\mu}$ is subjected to a magnetic field $\mathbf{B}$, there is a potential energy of interaction. The magnetic potential energy, E_{mag}, is given by

$$E_{\text{mag}} = -\boldsymbol{\mu} \cdot \mathbf{B} = -|\mu|\,|\mathbf{B}| \cos\theta \tag{16.3}$$

where the · between $\boldsymbol{\mu}$ and $\mathbf{B}$ specifies the dot product (or scalar product) of the two vectors, which is given by the second relationship in equation 16.3. The potential energy of interaction is a scalar, not a vector. And because of the $\cos\theta$ term in equation 16.3, the potential of interaction is at a minimum when the magnetic vectors are parallel, the potential is equal to zero when the magnetic vectors are perpendicular, and the potential is at a maximum when the vectors are directly opposed to each other (or *antiparallel*).

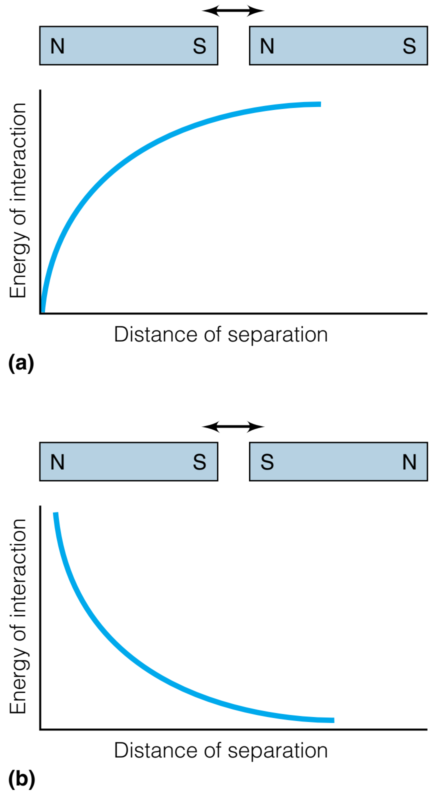

Figure 16.5 Interactions can be (a) attractive or (b) repulsive. Attractive interactions contribute to a lowering of the overall energy, whereas repulsive interactions contribute to an increase in the overall energy. The interactions of the two bar magnets shown mimic the interactions of magnetic fields and magnetic dipoles.

Example 16.3

Show that the units for magnetic field and magnetic dipole multiply together to yield units of energy. Use the fact that 1 T = 1 kg/(s^2·amp).

Solution

The $\cos\theta$ term has no units; it is simply a number. The magnitudes of $\boldsymbol{\mu}$ and $\mathbf{B}$ have the units amp·m^2 and T, respectively, so the unit of the interaction between them is, according to equation 16.3,

$$\text{amp} \cdot \text{m}^2 \cdot \text{T} = \frac{\text{amp} \cdot \text{m}^2 \cdot \text{kg}}{\text{s}^2 \cdot \text{amp}} = \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2} = \text{J}$$

J is the SI unit of energy. This illustrates that the interaction between magnetic dipoles and fields imposes an energy change on the system.

We have been assuming that electrical charges at the atomic (actually, subatomic) scale behave like macroscopic electrical currents. Actually, this is not the case, although the examples above illustrate that individual electrons can be treated like electrical currents. There is another presumption we have been using. We have been assuming a classical, *continuous* magnetic field. Because electromagnetism combines electricity and magnetism, and electricity is quantized (as electrons) and electromagnetic radiation is also quantized (as photons), we might expect that a quantum theory of magnetism would also be appropriate. Technically, this is indeed the case. However, most of the ideas we present in this chapter deal with the magnetic field as a classical phenomenon, not a quantum one. Only in the most advanced cases will a quantized magnetic field be considered.

Finally, we can relate the magnetic dipole to another quantity of quantum-mechanical importance: the angular momentum. Consider a particle with a charge of q moving around in a circle. It induces a magnetic dipole. If the particle has a linear velocity v in meters per second and is traveling in a circle having radius r meters, then the time necessary for one circular orbit is

$$\text{time} = \frac{2\pi r}{v}$$

Since current is defined as charge passing a point per second, the current I at any point in the particle's orbit is

$$I = \frac{Qv}{2\pi r}$$

where Q is the total charge passing by a point per second. The area of a circular orbit is πr^2. Combining the above equation with equation 16.2, one finds that the magnetic dipole of this particle is

$$\mu = |\boldsymbol{\mu}| = \frac{Qv}{2\pi r} \cdot \pi r^2 = \frac{Qvr}{2} \tag{16.4}$$

Remember that the definition of the angular momentum $\mathbf{L}$ is $\mathbf{L} = m\mathbf{r} \times \mathbf{v}$, or in our magnitude formalism, $L = |\mathbf{L}| = m|\mathbf{v}|\,|\mathbf{r}| = mvr$. Substituting, we find that

$$\mu = |\boldsymbol{\mu}| = \frac{Q}{2m}|\mathbf{L}| \tag{16.5}$$

where we have now tied the magnetic dipole of a particle in a circular orbit to its angular momentum. (By analogy, the vectors are also related: $\boldsymbol{\mu} = (Q/2m)\mathbf{L}$.)

For a single electron, the charge is $-e$, which equals -1.602×10^{-19} C. In this case, we have expressly included the minus sign on e because the electron is considered negatively charged. For a single electron, equation 16.5 is written as

$$\mu = |\boldsymbol{\mu}| = -\frac{e}{2m_e}|\mathbf{L}|$$

where m_e is the mass of an electron. Upon multiplying the last fraction by 1, written as $\hbar/\hbar$, we get

$$\mu = -\frac{e\hbar}{2m_e\hbar}|\mathbf{L}|$$

The *Bohr magneton,* μ_B, is defined as

$$\mu_B = \frac{e\hbar}{2m_e} \tag{16.6}$$

so that for an electron, the magnetic dipole can be written

$$\mu = -\frac{\mu_B}{\hbar}|\mathbf{L}| \tag{16.7}$$

Do not confuse the magnetic dipole, μ, for the symbol for the Bohr magneton, μ_B. The Bohr magneton has a value of about 9.274×10^{-24} J/T (joules per tesla). It (or similarly defined constants) is a necessary constant for almost all magnetic spectroscopies.

16.3 Zeeman Spectroscopy

One of the most straightforward and simple types of magnetic spectroscopy is called *Zeeman spectroscopy.* Its existence was proposed in 1890 by the Dutch physicist Hendrik Lorentz. If atoms were composed of electrical charges, Lorentz said, these charges should be affected by a magnetic field and a change would be noted in the atomic spectrum. In 1896 a student of Lorentz's, Pieter Zeeman, verified this prediction experimentally. For their work, Lorentz and Zeeman shared a 1902 Nobel Prize.

A simple example of the Zeeman effect is as follows: a single, sharp line in an atomic spectrum splits into three closely spaced, sharp lines when the sample is exposed to a magnetic field. The lines are extremely close: less than 1 cm^{-1} apart. However, the explanation for why the Zeeman effect occurs at all was left for quantum mechanics to explain.

For atoms, four quantum numbers describe the energy of an electron: n, ℓ, m_ℓ, and m_s. (All electrons have $s = \frac{1}{2}$.) For multielectronic atoms, however, there are more accurate quantum numbers, as explained in the last chapter: J, L, M_L, and M_S. The type and magnitude of Zeeman splitting depends on the possible values of certain of these quantum numbers.

If the electronic transitions involved in an allowed transition are *singlet states* (remember that for allowed transitions, $\Delta S = 0$), then magnetic effects on electronic spectra are determined exclusively by the orbital angular momentum, not the spin angular momentum. What is observed is the *normal Zeeman effect:* transitions are split as each L state separates into its $2L + 1$ possible different M_L values. This is illustrated for a $^1\text{S} \rightarrow {}^1\text{P}$ transition in Figure 16.6. The single transition that occurs without a magnetic field is split into a triplet of lines when a magnetic field is turned on. The selection rules are the same as for electronic transitions in multielectron atoms:

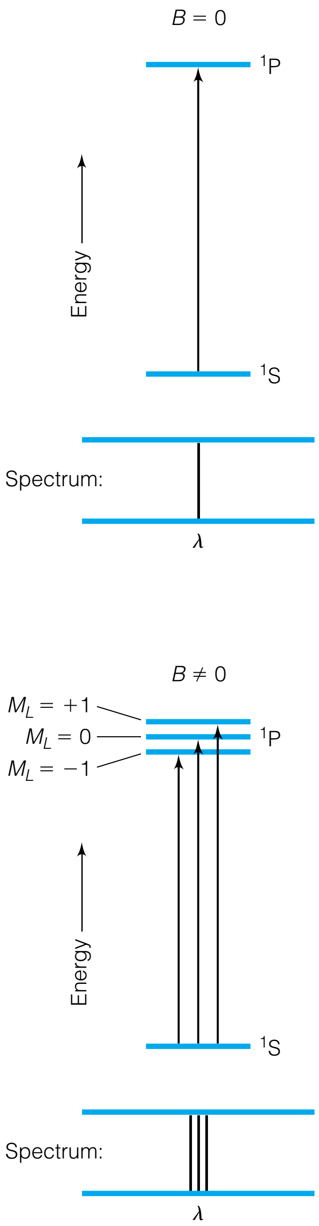

Figure 16.6 An example of the normal Zeeman effect. The $^1\text{S} \rightarrow {}^1\text{P}$ electronic transition is split into a triplet as a magnetic field separates the individual M_L levels in the ^1P excited state.

$$\Delta L = 0, \pm 1$$

$$\Delta S = 0$$

$$\Delta J = 0, \pm 1$$

$$\Delta M_L = 0, \pm 1 \quad (\text{but } M_L = 0 \not\longrightarrow M_L = 0 \text{ if } \Delta J = 0) \qquad \textbf{(16.8)}$$

The final exception ($M_L = 0$ does not change to a different state where M_L also equals 0 if $\Delta J = 0$) derives from the exact symmetry properties of the wavefunctions (as do all selection rules). Figure 16.6 is relatively simple, since only one of the states, the excited state, is splitting. The amount of the splitting—that is, the change in the energy of the state upon turning on the magnetic field—depends on the strength of the magnetic field B and the value of the z-component quantum number M_L and is given by

$$\Delta E_{\text{mag}} = \mu_{\text{B}} \cdot M_L \cdot B \qquad \textbf{(16.9)}$$

Since M_L can have positive or negative values or even be 0, the change in the energy can be positive, negative, or even zero.

Example 16.4

Calculate the splitting due to a magnetic field of 2.0 T on a $^1\text{S} \rightarrow {}^1\text{P}$ transition. Assume that only the ^1P state will split. (Why?)

Solution

The ^1S state will not split because it has $L = 0$ and so only $M_L = 0$. However, the ^1P state will split due to the presence of degenerate $M_L = -1$, 0, and $+1$ states. According to equation 16.9,

$$\Delta E_{\text{mag}}\,[M_L = -1] = (-1)(9.274 \times 10^{-24}\ \text{J/T})(2.0\ \text{T}) = -1.855 \times 10^{-24}\ \text{J}$$

The ΔE value in this case is *negative*. Convert this into units of cm^{-1} (using units of cm/s for the speed of light):

$$\frac{-1.855 \times 10^{-24}\ \text{J}}{(6.626 \times 10^{-34}\ \text{J·s})(2.9979 \times 10^{10}\ \text{cm/s})} = -0.9338\ \text{cm}^{-1}$$

The energy of the transition decreases by just under one wavenumber due to the presence of the magnetic field. $\Delta E_{\text{mag}}\,[M_L = 0]$ will be zero because $M_L = 0$. The $\Delta E_{\text{mag}}\,[M_L = +1]$ will have the same magnitude as the transition to $M_L = -1$, except it will have the opposite sign. Therefore (and without the need to do any additional math),

$$\Delta E_{\text{mag}}\,[M_L = +1] = +0.9338\ \text{cm}^{-1}$$

The transition will turn into a triplet of equally spaced lines. Thus, the Zeeman spectrum of this transition will resemble Figure 16.6.

The fact that a single line turns into a trio of lines in the above example is characteristic of a $^1\text{S} \rightarrow {}^1\text{P}$ transition. Therefore, the normal Zeeman effect gives spectroscopists clues about the term symbols of the states involved in atomic spectra. Each combination of term symbols has, for $S = 0$, a certain number of allowed transitions that is characteristic of the transition, thanks to quantum numbers. This information is useful for identifying the quantum numbers of ground and excited states, which is a crucial part of the understanding of atomic and molecular structure in the quantum-mechanical formalism.

In cases where $S \neq 0$, we do not have a singlet state, and the total angular momentum quantum number J must be considered. (In the previous case, $J = L$.) In this case, magnetic effects on an electronic spectrum are determined not only by the orbital angular momentum but by the spin angular momentum as well. The spin of an electron also induces a magnetic dipole, whose value is similar to equation 16.7, but because spin angular momentum is nonclassical, there is another term in the expression. The spin magnetic dipole $\mathbf{m}$ has a magnitude m (not to be confused with the quantum number for the z component of orbital angular momentum of

$$m = -g_e \frac{\mu_B}{\hbar} |\mathbf{S}| \tag{16.10}$$

where g_e is a pure number (that is, no units) called the *electron g factor* and equals 2.002319304 . . . for a free electron. It is slightly different for bound electrons, but not enough for concern at this point. It is almost equal to exactly 2 (and is sometimes approximated as 2), and the reasons it is not exactly 2 are perhaps worth researching on your own. Regardless, the g factor is a necessary addition in order to explain the effects of electron spin and its magnetic dipole.

For nonsinglet states, *all* of the good quantum numbers—J, S, L, and M_J—affect the change in energy of the electronic energy levels. However, because the pattern of the changes is more complicated, the effect of a magnetic field on nonsinglet electronic states is called the *anomalous Zeeman effect.* The change in the electronic energy levels due to the imposition of a magnetic field of strength B is given by

$$\Delta E_{\text{mag}} = g_J \cdot \mu_{\text{B}} \cdot M_J \cdot B \tag{16.11}$$

where g_J is called the *Landé g factor.* It depends on J, L, and S and is related to g_e by the expression

$$g_J = 1 + \left[\frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}\right](g_e - 1) \tag{16.12}$$

To a very, very good approximation, $g_e - 1 \approx 1$, so equation 16.12 is sometimes written as

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \tag{16.13}$$

This simplified version of g_J is off by only about 0.1% from the expression in equation 16.12. The selection rules in terms of J, L, M_L, and S in equation 16.8 above apply. The Landé g factor is named after Alfred Landé, a German scientist who in 1923 (before the development of quantum mechanics) derived equation 16.13 from a visual inspection of a lot of atomic spectra.

Figure 16.7 shows a simple electronic spectrum with and without a magnetic field as an example of the anomalous Zeeman effect. Notice that the splitting of the lines when the sample is exposed to a magnetic field isn't as simple as with the normal Zeeman effect. This is one reason it was considered anomalous.

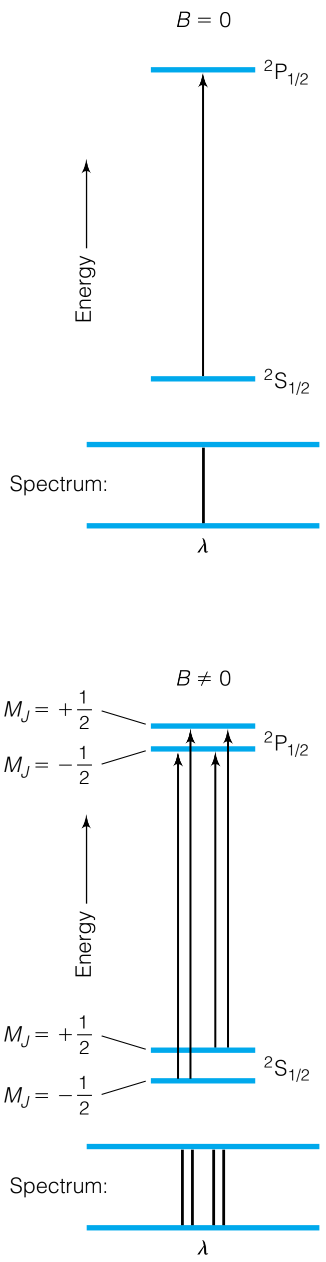

Figure 16.7 When $J \neq L$ (that is, when $S \neq 0$), the splitting due to a magnetic field is more complicated and is called the anomalous Zeeman effect. The figure shows a transition in the absence and in the presence of a magnetic field.

16.4 Electron Spin Resonance

Normally, molecules composed of main-group elements have a ground state where all of the electrons are spin-paired.* Compounds having all-spin-paired electrons show no noteworthy magnetic effects in the electronic spectrum due to spin magnetic dipoles.

In molecules that have unpaired electrons, such as d-block and f-block compounds as well as free radical species, there is a net spin magnetic dipole. In the presence of a magnetic field, the presence of a spin magnetic dipole creates a potential energy of interaction, given by equation 16.11. When a single electron is involved (as is usually the case for main-group free radicals), the total spin vector **S** is simply $\frac{1}{2}$, and the potential energy of interaction can be rewritten in terms of the m_s quantum number, which is either $+\frac{1}{2}$ or $-\frac{1}{2}$. In terms of m_s,

$$\Delta E_{\text{mag}} = g_e \cdot \mu_B \cdot m_s \cdot B \tag{16.14}$$

where the g factor for a free electron, g_e, is used instead of g_J, and m_s can be either $+\frac{1}{2}$ or $-\frac{1}{2}$. This implies a relatively simple two-level system where the $m_s = +\frac{1}{2}$ state goes up in energy and the $m_s = -\frac{1}{2}$ state goes down in energy. Such a system is illustrated in Figure 16.8. The difference between the two energy levels is equal to $g_e\mu_B B$.

What is the difference between equations 16.14 and 16.11? In equation 16.14, we are considering the effect on one electron, whereas equation 16.11 is a more general case with more than one electron. For a single electron, the magnetic field effects are determined by m_s, whereas for multiple electrons the effects are better described by J and M_J. Therefore, for multiple electrons g_J and M_J are the appropriate variables, and for a single electron g_e and m_s are the relevant variables.

The splitting of the two spin states for the unpaired electron is not a lot in terms of energy: using equation 16.14, one can see that the splitting between the two is equal to 1.855×10^{-23} J/tesla, or about 0.934 cm^{-1} per tesla. If one wanted to irradiate a sample having an unpaired electron and exposed to a magnetic field, then radiation of the proper wavelength would cause an electron lying in a lower, $m_s = -\frac{1}{2}$ state to absorb radiation and move to the upper, $m_s = +\frac{1}{2}$ state. When the magnetic-interaction-induced difference in energy of the two states equals the energy of the photon, absorption of a photon can occur and we say that a state of *resonance* is established. The relevant equation is

$$\tilde{\nu}_{\text{res}} = \frac{g_e \mu_B B}{hc} \tag{16.15}$$

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*NO and NO_2 are two of the rare exceptions to this statement, each having an odd number of electrons. The ground state of O_2 has two unpaired electrons in degenerate molecular orbitals, as explained in Chapter 12.

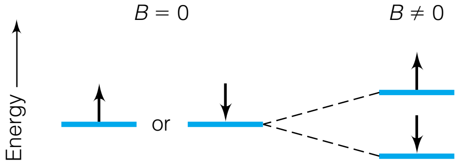

Figure 16.8 In the absence of a magnetic field (left), an unpaired electron of a free radical has the same energy no matter what direction its spin. However, in the presence of a magnetic field (right), the two spin directions have different energies, and electromagnetic radiation can cause a transition between the two energy levels.

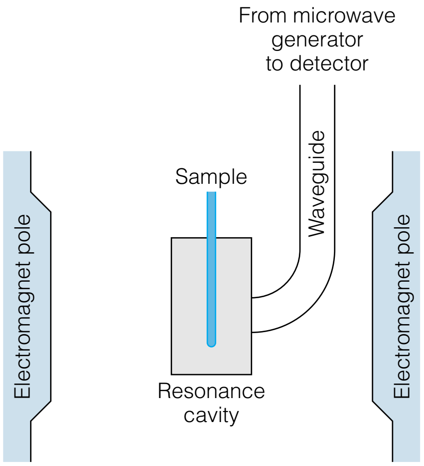

Figure 16.9 A diagram of an ESR spectrometer. A sample is exposed to microwaves of known wavelength, and a slowly varying magnetic field is applied. When the resonance condition is established, microwaves are absorbed and the transition from ground state to excited state occurs. The spectrometer detects the absorption of the microwaves to generate the spectrum.

where $\tilde{\nu}_{\text{res}}$ is the frequency of the absorbed light *in units of wavenumbers, h* is Planck's constant, c is the speed of light in units of cm/s, g_e is the electron g factor, μ_B is the Bohr magneton, and B is the magnetic field strength in units of T. *In units of* s^{-1} or Hz, the equation is rewritten as

$$\nu_{\text{res}} = \frac{g_e \mu_B B}{h} \tag{16.16}$$

Given the magnetic field strengths that are available in most laboratory instruments today (~0.3 T), the transitions due to the splitting of the electron spin states occur in the microwave region of the spectrum (whose frequencies are usually expressed in units of gigahertz, or GHz). Control of microwaves is relatively straightforward, and spectrometers are readily available that take advantage of the resonance condition. Spectroscopy based on this method is called *electron spin resonance,* or ESR, spectroscopy. A schematic diagram of an ESR spectrometer is shown in Figure 16.9.

Example 16.5

In a 0.35-T magnetic field, what is the expected frequency, in GHz, of a free electron $m_s = -\frac{1}{2} \rightarrow m_s = +\frac{1}{2}$ transition?

Solution

Using equation 16.16:

$$\nu_{\text{res}} = \frac{(2.002)(9.274 \times 10^{-24}\ \text{J/T})(0.35\ \text{T})}{(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})} = 9.81 \times 10^{9}\ \text{s}^{-1} = 9.81\ \text{GHz}$$

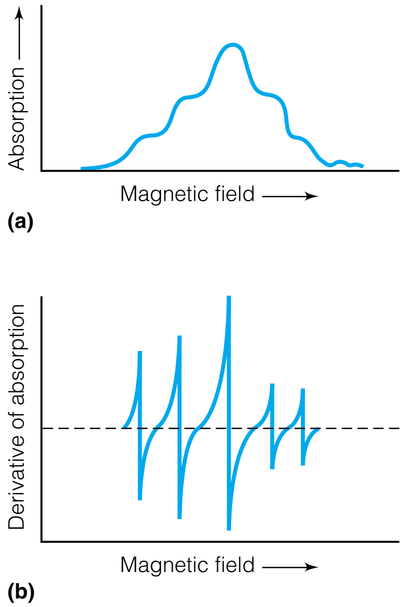

Figure 16.10 (a) ESR spectra plotted as an absorption spectrum show multiple, unresolved absorptions. Such spectra are difficult to interpret. (b) ESR spectra plotted as derivative spectra are easier to interpret, because the individual peaks are more easily resolved.

Example 16.6

What magnetic field is necessary for an $m_s = -\frac{1}{2} \rightarrow m_s = +\frac{1}{2}$ transition to be in resonance with microwave radiation having a wavelength of 11.8 cm? (This is the approximate wavelength of the microwaves that are used in some microwave ovens.)

Solution

A λ of 11.8 cm implies a wavenumber $\tilde{\nu}$ of 1/11.8 cm = 0.0847 cm^{-1}. Using equation 16.15, we get

$$0.0847\ \text{cm}^{-1} = \frac{(2.002)(9.274 \times 10^{-24}\ \text{J/T})B}{(6.626 \times 10^{-34}\text{J}\cdot\text{s})(2.9979 \times 10^{10}\ \text{cm/s})}$$

where we have used the value for the speed of light in units of cm/s and the magnetic field strength, B, is the only unknown. Solving for B:

$$B = 0.0906\ \text{T} = 906\ \text{G}$$

This is a relatively weak magnetic field, although it is more than 1000 times Earth's magnetic field.

ESR spectra are usually collected by radiating a sample with monochromatic microwave radiation and then varying the magnetic field. It is easier to do this than to hold the magnetic field constant and vary the frequency of the microwave radiation. In either case, a resonance condition can be established. Many (but not all) ESR spectra are a conglomeration of closely spaced, unresolved lines; see Figure 16.10a. To emphasize the exact positions of the different absorptions, it is conventional to plot an ESR spectrum as a *derivative* of the absorption with respect to the varying magnetic field. In this way, the different absorptions are enhanced. Figure 16.10b shows the derivative spectrum of the absorption spectrum in Figure 16.10a. It is much easier to interpret a spectrum like Figure 16.10b than one like Figure 16.10a (although they contain the same information).

The above discussion may lead one to think that all electrons absorb the same microwave radiation at a particular magnetic field. If this were so, then ESR spectroscopy would have limited use. However, such is not the case. The exact value of the g factor g_e depends strongly on the local environment of the unpaired electron. This means that the exact frequency of resonant absorption depends on the specific molecule of interest. In particular, because nuclei themselves also have a spin, there is an interaction, or a *coupling*, between the unpaired electron's spin and the spin angular momentum of the individual nucleus, which is labeled I.

In a molecule having several nuclei with nonzero spin, the nuclear spins can couple to give a total molecular nuclear spin $M_{I,\text{mol}}$ given by

$$M_{I,\text{mol}} = \sum_{\text{nuclei}} M_I$$

where M_I is the spin of an individual nucleus. The molecule has $2M_{I,\text{mol}} + 1$ possible orientations of the total nuclear spin in the z dimension, $M_{I,z}$. Each orientation couples differently with an unpaired electron. This type of coupling is called *hyperfine coupling*. Because nuclear spin states are quantized (as with any angular momentum), the interaction energies are also quantized and relatively evenly spaced. It is easy to define a *hyperfine coupling constant a,* having units of T (tesla), such that

$$B_{\text{local environment}} = B_{\text{mag field}} + a \cdot M_{I,z} \tag{16.17}$$

The local environment magnetic field B is thus slightly different than the imposed magnetic field B by some quantized multiple of the hyperfine coupling constant. Hyperfine coupling constants are typically on the order of millitesla, but they are large enough to detect in modern ESR spectroscopy. Figure 16.11 shows an ESR spectrum with a well-defined hyperfine coupling constant. The hyperfine coupling constant is useful in that the ESR spectrum can indicate what atom or atoms (since atoms have specific nuclear spins) the unpaired electron is "on."

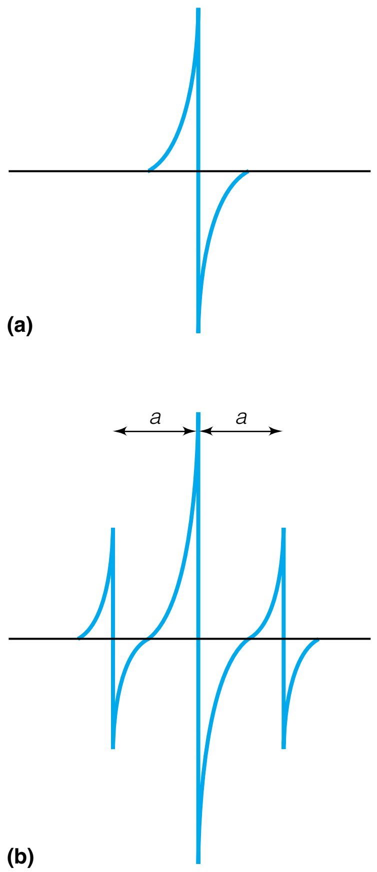

Figure 16.11 (a) An unpaired electron on an atom having a nuclear spin of zero shows a single absorption in an ESR spectrum. However, (b) an electron on an atom having a nonzero nuclear spin shows multiple absorptions due to the interaction of the electron spin and the nuclear spin. This interaction is called hyperfine coupling. The amount of coupling is measured by the hyperfine coupling constant, a. Here, the electron is on an atom having $I = 1$.

Example 16.7

How many ESR peaks would be present due to a single unpaired electron on each of the following? (Use the fact that the nuclear spins of H, N, and P are, respectively, $\frac{1}{2}$, 1, and $\frac{1}{2}$.)

a. A hydrogen atom
b. An NH_3 radical
c. A PH_3 radical

Solution

a. A single hydrogen atom has two possible M_I values: $+\frac{1}{2}$ and $-\frac{1}{2}$. It will therefore have two different local magnetic fields (depending on the value of M_I), and so will have two ESR absorptions due to hyperfine coupling.
b. The combination of the single N atom's spin of 1 and the three hydrogen atoms' spins of $\frac{1}{2}$ means a value of $M_{I,\text{mol}}$ of $\frac{5}{2}$. Therefore, the z component of the combined nuclear spins, $M_{I,z}$, can range from $+\frac{5}{2}$ to $-\frac{5}{2}$. There are six possible $M_{I,z}$ values and so six ESR absorptions.
c. Similar to part b, the possible total z-component nuclear spins range from $+2$ to -2 in integral steps, for a total of five possible $M_{I,z}$ values. This indicates five possible values for the local magnetic field, yielding five ESR absorptions.

The number of first-derivative peaks seen in an ESR spectrum can provide a lot of information about a molecule's structure, because in a molecule any atom that has a nuclear magnetic moment contributes to the hyperfine coupling. Consider the methyl radical, $CH_3\cdot$. The carbon nucleus has $I = 0$ and so does not contribute to the ESR hyperfine splitting. The three hydrogen atoms each have $I = \frac{1}{2}$, and the possible combinations of the nuclear spins $M_{I,z}$ are $+\frac{3}{2}$ (all three nuclear spins in the $+\frac{1}{2}$ direction), $+\frac{1}{2}$, $-\frac{1}{2}$, and $-\frac{3}{2}$ (all three nuclear spins in the $-\frac{1}{2}$ direction). Therefore, four lines are expected in the ESR spectrum of the methyl radical, and that is what is seen experimentally. Similarly, for the benzene radical anion there are seven distinct lines in the ESR spectrum due to the six protons. Nonequivalent nuclei contribute differently to the hyperfine coupling. Therefore, ESR spectra for polyatomic molecules can quickly get complicated, but extracting the proper information from them provides quite a bit of detail about the structure of the ESR-active species.

Example 16.8

In an ESR experiment where the microwave radiation was fixed at 10.0 GHz, the $M_{I,z} = +\frac{1}{2}$ absorption of an ESR spectrum of the methyl radical appears at a magnetic field strength of 0.3376 T, and the $M_{I,z} = -\frac{1}{2}$ absorption appears at 0.3353 T. Calculate the hyperfine coupling constant *a* and predict the position of the other two absorptions expected for the $M_{I,z} = -\frac{3}{2}$ and the $M_{I,z} = +\frac{3}{2}$ absorptions.

Solution

The following two equations, based on equation 16.17, need to be satisfied:

$$0.3376\ \text{T} = B_{\text{mag field}} + a \cdot +\tfrac{1}{2}$$

$$0.3353\ \text{T} = B_{\text{mag field}} + a \cdot -\tfrac{1}{2}$$

There are two equations and two unknowns. They can be solved simultaneously using simple linear algebra techniques (that is, substitution). Upon doing so, one finds a value of $a = 0.0023\ \text{T} = 23\ \text{G}$, as well as a $B_{\text{mag field}}$ of 0.3366 T. Using equation 16.17, we can predict the absorptions for $M_{I,z} = -\frac{3}{2}$ and $M_{I,z} = +\frac{3}{2}$ as

$$0.3366\ \text{T} + (0.0023\ \text{T})(+\tfrac{3}{2}) = 0.3401\ \text{T} \quad \text{for } M_{I,z} = +\tfrac{3}{2}$$

$$0.3366\ \text{T} + (0.0023\ \text{T})(-\tfrac{3}{2}) = 0.3332\ \text{T} \quad \text{for } M_{I,z} = -\tfrac{3}{2}$$

Four equally spaced lines are expected.

Figure 16.12 The ESR spectrum of the CF_3 radical, showing the complexity due to hyperfine coupling. The cluster of tiny signals in the center is an impurity. *Source:* M. T. Rogers and L. D. Kispert, *J. Chem. Phys.*, 1967, 46: 3193.

Nonequivalent nuclei make a different contribution to the hyperfine splitting. If a nucleus having spin *I* and a different nucleus having spin *J* are in a molecule, then one can expect up to $(2I + 1)(2J + 1)$ separate absorptions in the ESR spectrum. In some cases, lines lie practically on top of each other and are unresolved, so that fewer lines than expected are seen. ESR spectra can get complicated. Figure 16.12 shows an example of an ESR spectrum of a relatively simple compound.

In many organic molecules, the *g* factor of the electron is about 2. However, unpaired electrons are also present in many metal compounds, especially metal compounds having atoms of transition metal or lanthanide or actinide elements. These unpaired electrons are from *d* or *f* orbitals, and the molecules are not considered free radicals. However, the unpaired electrons do give rise to signals via a resonance phenomenon. Metals having unpaired electrons in *d* or *f* orbitals are paramagnetic, so when the magnetic resonance technique is applied to such compounds, it is called *electron paramagnetic resonance*, or EPR. Although the general ideas behind the technique are similar, the *g* values are different, up to about 4 in some transition metal complexes. Different microwave regions are used, depending on the *g* factor, magnetic field strength available, resolution, and other factors. Microwave frequencies at about 9.5 GHz, 24 GHz, and 35 GHz are common. Magnetic field strengths must be consistent with equation 16.11 in order for resonance to occur.

16.5 Nuclear Magnetic Resonance

We considered electron spin resonance spectroscopy before nuclear magnetic resonance spectroscopy because ESR deals primarily with the subatomic particles most popular in our treatment of quantum mechanics: the electrons. However, atoms also have nuclei, which have many of the same properties that electrons have. In particular, many nuclei also have a total spin and a magnetic dipole.

Although we recognize that nuclei are composed of individual nuclear particles (protons and neutrons), from our perspective it is simplest to think of a nucleus as a single particle that has properties determined by all of the nuclear particles together. A nucleus therefore has a certain total charge, which is typically denoted Z. A nucleus also has a total spin angular momentum, which in the previous section was denoted I. The total spin angular momentum ("spin") of a nucleus is determined by the number and pairing of the individual nuclear particles (whose angular momenta interact using rules similar to those that govern electrons, but they are not the same and will not be considered here). For example, the hydrogen nucleus, a single proton, has a nuclear spin I of $\frac{1}{2}$. A deuterium nucleus has a nuclear spin of 1, and a tritium nucleus has a spin of $\frac{1}{2}$. ^{12}C has a nuclear spin of 0, and ^{13}C has a nuclear spin of $\frac{1}{2}$. The metastable isotope ^{134}Cs, which is radioactive and has a half-life of 2.90 hours, has an I of 8, the largest of any atomic nucleus.

Nuclear spins behave like electron spins in that there is a quantized value for the total spin, and a quantized value for the z component of the total spin, symbolized by M_I. (We used this idea in the previous section.) For our purposes, it is important to recognize that, just like one or more electrons in an atom, a nucleus having a nonzero spin has a magnetic dipole associated with it. A *nuclear magnetic dipole* can be defined, similarly to the electron's magnetic dipole. Starting with the smallest nucleus, that of the hydrogen atom, we have the nuclear magnetic dipole of the proton, which is given as

$$\mu_p = g_p \frac{e}{2m_p}\mathbf{I}_p \qquad \textbf{(16.18)}$$

which, when multiplied by $\hbar/\hbar$, becomes analogous to equation 16.10 for electrons. Here, $\mathbf{I}_p$ is the total spin angular momentum of the proton, which follows the normal quantum-mechanical rules for total angular momentum: $I_p^2 = I(I+1)\hbar^2$, so $I_p = \sqrt{I(I+1)}\hbar$. Equation 16.18 also allows us to define an analogous magneton called the *nuclear magneton* μ_N:

$$\mu_N = \frac{e\hbar}{2m_p} \qquad \textbf{(16.19)}$$

where e is the charge on the proton ($+1.602 \times 10^{-19}$ C) and m_p is the mass of the proton (1.673×10^{-27} kg). This nuclear magneton has a value of about 5.051×10^{-27} J/T and is used to determine energy changes for all nuclei, not just the proton. The g_p in equation 16.18 is the g factor for the proton, and (for reasons we won't go into) has a value of 5.586. Other nuclei have their own characteristic values for g_N. The nuclear magnetic moment of a single proton is about 2.443×10^{-26} J/T.

Example 16.9

Compare the relative magnitudes of the electron's magnetic moment and the proton's magnetic moment. Why are they different?

Solution

The magnetic moment of the hydrogen atom nucleus, a proton, is 2.443×10^{-26} J/T. The electronic magnetic moment is found by using equation 16.10:

$$m = -g_e\frac{\mu_B}{\hbar}|\mathbf{S}| = -g_e\frac{\mu_B}{\hbar}\hbar\sqrt{\frac{1}{2}\left(\frac{3}{2}\right)}$$

$$= -2.002\frac{(9.274 \times 10^{-24}\ \text{J/T})}{(6.626 \times 10^{-34}\ \text{J·s})/2\pi} \cdot \frac{6.626 \times 10^{-34}\ \text{J·s})}{2\pi}\sqrt{\frac{3}{4}}$$

$$= -2.002(9.274 \times 10^{-24}\ \text{J/T})\sqrt{\frac{3}{4}}$$

where we have used the fact that $|\mathbf{S}| = \sqrt{S^2} = \sqrt{\frac{1}{2}(\frac{1}{2}+1)\hbar^2} = \hbar\sqrt{\frac{3}{4}}$. The magnetic moment of an electron is thus $(-)1.608 \times 10^{-23}$ J/T. (It is negative, but in many cases the absolute value of the magnetic moment is used, so the negative sign is ignored.) The two reasons for the difference in the magnetic moments are the different g factors and the different masses of the particles.

Because certain nuclei have a magnetic dipole, they experience a potential energy when they are subjected to a magnetic field. As with electrons, there are $2I + 1$ different possible orientations of the nuclear spin when subjected to a magnetic field, and each orientation has its own change in total energy ΔE_{mag}. In the presence of a magnetic field, then, these different potential energies split into individual levels, and electromagnetic radiation of just the right energy can cause a nucleus to go from one nuclear-spin orientation to another. The change in the energy is similar to that for ESR:

$$\Delta E_{\text{mag}} = g_N \cdot \mu_N \cdot B \cdot M_I \qquad \textbf{(16.20)}$$

where g_N is the g factor for the particular nucleus, μ_N is the nuclear magneton, B is the magnetic field strength, and M_I is the quantum number for the z component of the nuclear angular momentum, which can have $2I + 1$ possible values. We are using M_I instead of $M_{I,z}$ because we are now considering only a single nucleus, not a combination of different atomic nuclei. Note how equation 16.20 is similar to equation 16.14. Table 16.1 lists the nuclear properties g_N and I for various nuclei. Figure 16.13 shows the splitting of the M_I nuclear levels for nuclei having $I = 3$ and exposed to a magnetic field.

Table 16.1 Two properties of various nuclei

Nucleus	Spin, I	Nuclear g factor, g_N
^{1}H	$\frac{1}{2}$	5.586
^{3}He	$\frac{1}{2}$	−4.2548
^{6}Li	1	0.8220
^{11}B	$\frac{3}{2}$	1.7923
^{13}C	$\frac{1}{2}$	1.405
^{19}F	$\frac{1}{2}$	5.2567
^{31}P	$\frac{1}{2}$	2.2634
^{209}Bi	$\frac{9}{2}$	0.8975

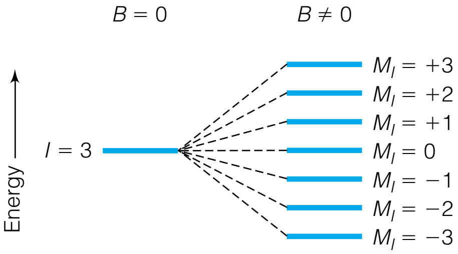

Figure 16.13 In the presence of magnetic fields, nuclear spin states split into nondegenerate energy levels. NMR spectroscopy probes the transitions between these nuclear energy states.

Because different nuclei have different nuclear spins I and different possible z components of the nuclear spins M_I, you might think that a specific formula for the expected energies of transitions would be difficult to determine, but that is not the case. There is a selection rule regarding changes in the M_I quantum number:

$$\Delta M_I = \pm 1 \qquad \textbf{(16.21)}$$

and for absorption spectra it becomes simply $\Delta M_I = +1$. (We did not formally consider a selection rule for ESR transitions.) Using this fact, we can come up with equations similar to equations 16.15 and 16.16 to relate the resonant frequency or wavelength of light that will be absorbed by a nucleus in a magnetic field. They are

$$\tilde{\nu}_{\text{res}} = \frac{g_N\mu_N B}{hc} \quad (\text{in cm}^{-1}) \qquad \textbf{(16.22)}$$

$$\nu_{\text{res}} = \frac{g_N\mu_N B}{h} \quad (\text{in s}^{-1}) \qquad \textbf{(16.23)}$$

where all of the variables have previously been defined. The first equation yields a wavelength in units of wavenumbers, and the second equation gives units of s^{-1}. Spectroscopy based on the splitting of the M_I levels of nuclei by a magnetic field is called *nuclear magnetic resonance*, or NMR, spectroscopy. NMR spectroscopy was developed largely by the efforts of Felix Bloch at Stanford University and Edward Purcell at Harvard University in 1946. They shared a 1952 Nobel Prize for their efforts.

Example 16.10

Predict the wavelength of transition for an ^{19}F nucleus exposed to a magnetic field of 7730 G. ^{19}F has a nuclear spin of $\frac{1}{2}$ and a g_N of 5.2567. Use the nuclear magneton μ_N.

Solution

Since $I = \frac{1}{2}$, the only possible values of M_I are $+\frac{1}{2}$ and $-\frac{1}{2}$, and the only possible transition is $M_I = -\frac{1}{2} \rightarrow M_I = +\frac{1}{2}$. Using equation 16.23, we find

$$\nu_{\text{res}} = \frac{g_N \mu_N B}{h} = \frac{(5.2567)(5.051 \times 10^{-27}\ \text{J/T})(7730\ \text{G})}{6.626 \times 10^{-34}\ \text{J·s}} \cdot \frac{1\ \text{T}}{10{,}000\ \text{G}}$$

$$\nu_{\text{res}} = 3.098 \times 10^{7}\ \text{Hz} = 30.98\ \text{MHz}$$

This is in the radio wave region of the electromagnetic spectrum.

Instead of using nuclear g factors, a *magnetogyric ratio* γ can be defined as the proportionality constant between the nuclear magnetic moment's z component and the M_I quantum number:

$$\mu_z = \gamma \cdot \hbar \cdot M_I \tag{16.24}$$

The relationship between the magnetogyric ratio and the nuclear g factor is

$$\gamma = \frac{g_N \cdot \mu_N}{\hbar} \tag{16.25}$$

NMR would be useless if all nuclei of the same element absorbed the same frequency of light at some particular magnetic field strength (except perhaps for elemental analysis). However, the local electronic environment around nuclei cause different atomic nuclei to experience a slightly different total magnetic field. This is because the electrons are also affected by the magnetic field. (This should be obvious from our earlier treatment of ESR spectroscopy.) In a particular chemical environment, the total magnetic field experienced by a nucleus is the sum of B plus an additional, small magnetic field induced by B on the electrons. The additional magnetic field, ΔB, is proportional to B and is given by the expression

$$\Delta B = -\sigma B \tag{16.26}$$

where σ is a dimensionless constant called the *shielding constant*. The total magnetic field experienced by a nucleus is therefore

$$B_{\text{tot}} = B - \sigma B = B(1 - \sigma) \tag{16.27}$$

The exact frequency of light that is absorbed depends on the *total* magnetic field, B_{tot}, not the applied magnetic field B. Shielding constants themselves are very small, on the order of 1 to 3×10^{-5}. Their existence was first demonstrated by W. D. Knight in 1949, not long after the development of nuclear magnetic resonance itself.

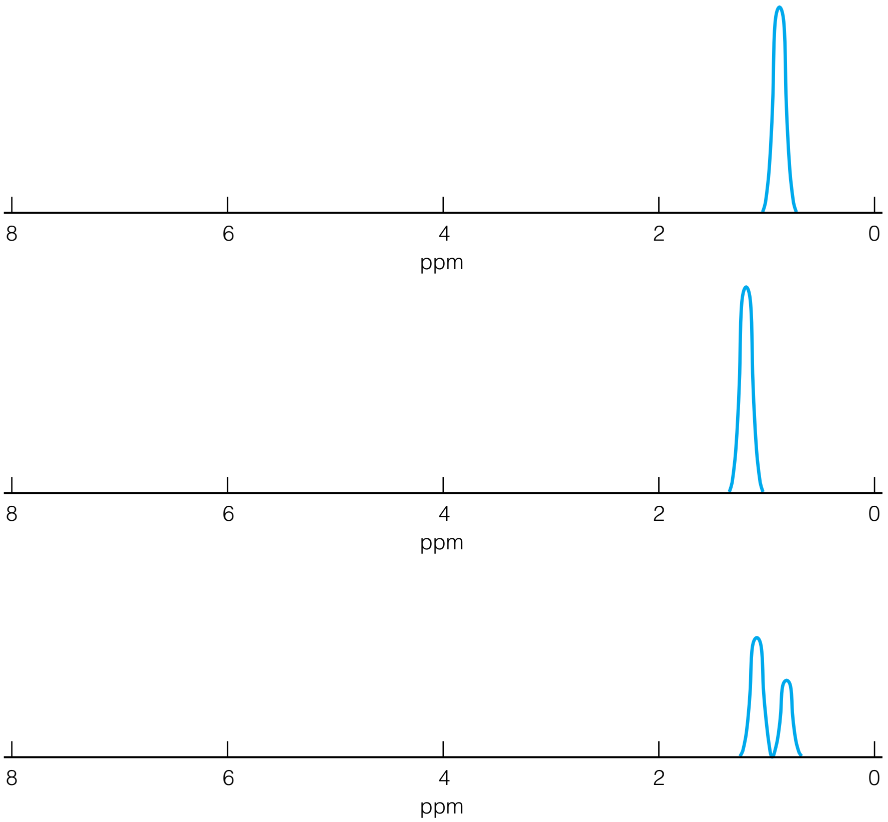

Figure 16.14 The NMR spectra of the first three alkanes shows that the protons on "different" carbons absorb at different points. This is part of the value of NMR spectroscopy.

What equation 16.27 implies is that different nuclei of the same element experience different total magnetic fields due to their chemical environment, and so will absorb at slightly different frequencies of radiation. This is best illustrated by an example such as that in Figure 16.14. The four hydrogen atoms in methane, CH_4, are chemically equivalent. Therefore, they will absorb the same frequency of radiation in an NMR experiment. The six hydrogens in ethane, CH_3CH_3, are also chemically equivalent and so will also absorb the same frequency of radiation. However, the protons in propane, $CH_3CH_2CH_3$, are not all chemically equivalent. The hydrogens on the end carbons are equivalent to each other, but the hydrogens in the middle methylene carbon are in a different chemical environment than the methyl carbons. They will experience a slightly different total magnetic field, and so will absorb a different frequency of radiation. This will lead to two separate absorptions in an NMR spectrum, one for each type of hydrogen (at least in a low-resolution NMR spectrum). In this manner, structural information about a molecule begins to be obtained.

Example 16.11

How many chemically different hydrogens in each of the following, and how many NMR absorptions would be expected?

a. Benzene, C_6H_6

b. Toluene, $C_6H_5CH_3$

Solution

a. The benzene molecule is highly symmetric, and all its hydrogens are environmentally equivalent. Therefore, only a single absorption is expected.

b. The addition of a methyl group to the benzene ring changes the environments of the hydrogens on the ring. Two hydrogens are on the carbon nearest to the methyl group, two are on the carbons next removed, and one hydrogen is directly opposite it. Also, three equivalent hydrogens are on the methyl group itself, assuming that the methyl group is free to rotate. Therefore, toluene has four chemically different hydrogens, and one would expect four absorptions in the NMR spectrum.

A conceptual diagram of an absorption-type NMR spectrometer is shown in Figure 16.15. The magnetic field strength is usually between 1 and 10 teslas, depending on the model of spectrometer. Experimentally, it is more convenient to fix the radio frequency and change the magnetic field strength until resonance conditions are established, and monitor the absorption of the radio waves versus field strength. A typical low-resolution NMR is shown in Figure 16.16. NMR spectra that detect absorption by hydrogen nuclei are called proton NMR or ^{1}H NMR spectra. It is typical to measure an NMR spectrum using some standard reference material as an internal calibration compound, and plot the values of B_{tot} for the environmentally different nuclei with respect to the internal standard. For ^{1}H NMR, tetramethylsilane (TMS), $\text{Si(CH}_3)_4$, is used as an internal standard. This compound has a very high shielding constant; most compounds have lower shielding constants than TMS. The difference between the shielding constant of TMS and another compound is called the *chemical shift*, labeled δ. Since shielding constants have values in the 10^{-5} to 10^{-6} gauss range, it is common to multiply the difference in shielding constants by 10^6 to yield manageable numbers. In such cases, the chemical shift is said to have units of *parts per million* (ppm):

$$\delta \text{ (in ppm)} = (\sigma_{\text{TMS}} - \sigma_{\text{nucleus}}) \times 10^6 \qquad \textbf{(16.28)}$$

Figure 16.17 shows a low-resolution NMR spectrum in terms of δ.

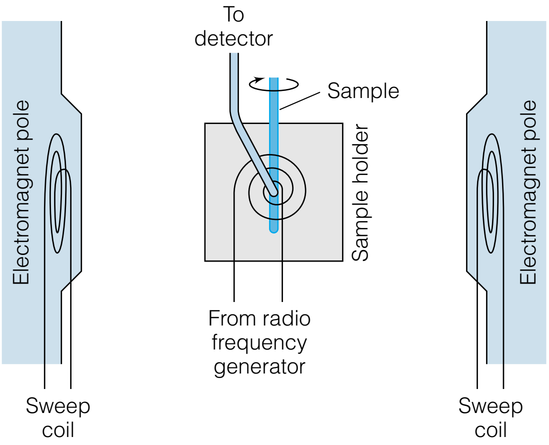

Figure 16.15 A diagram of a standard NMR spectrometer. The sweep coils vary the magnetic field in small amounts while radio waves bombard the sample. Any absorption of radio waves will be detected by the detector circuit. The samples are usually spun to minimize inhomogeneities.

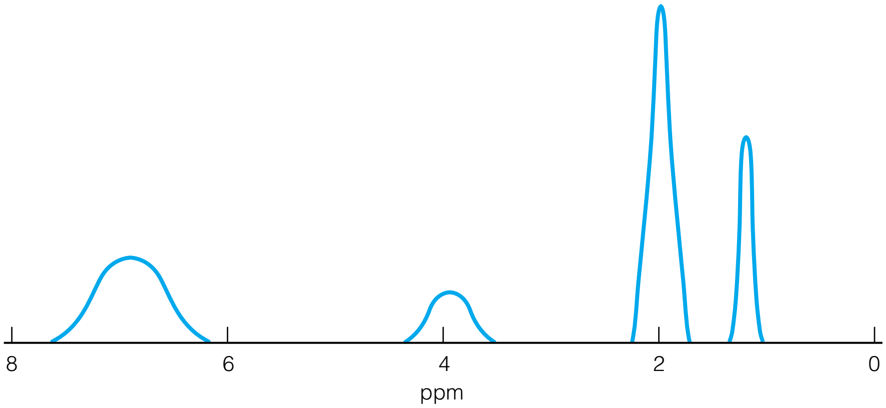

Figure 16.16 A typical low-resolution NMR spectrum of *p*-acetophenetidide, a simple disubstituted benzene derivative that has several chemically different hydrogens.

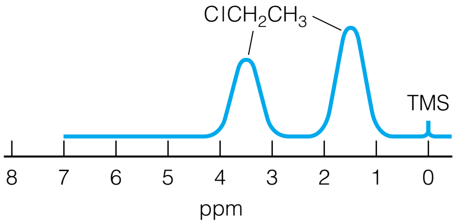

Figure 16.17 NMR absorptions are typically measured in units of parts per million, which ultimately refer to the chemical shift of the particular nucleus in gauss units.

Higher-resolution NMR spectra provide even more information about the structure of a molecule. This is because nuclei that have magnetic moments can interact, or *couple,* with each other. (The mechanism of coupling is actually through the electrons surrounding the nuclei, but we will not go into that here.) Since a magnetic moment is caused by the nonzero spin of a nucleus, this effect is called *spin-spin coupling,* and its magnitude is given by a *spin-spin coupling constant* between nucleus *i* and nucleus *j*, labeled J_{ij}. The J_{ij} values have units of Hz. The net effect of spin-spin coupling is to split an absorption into multiple individual absorptions, much like the Zeeman effect splits electronic absorptions. Figure 16.18 shows an example of spin-spin coupling on an NMR spectrum. Internuclear interactions fall off rapidly with distance. For organic compounds, most C and O atoms have a zero nuclear spin and so do not contribute to spin-spin coupling. Only hydrogen atoms will interact with other

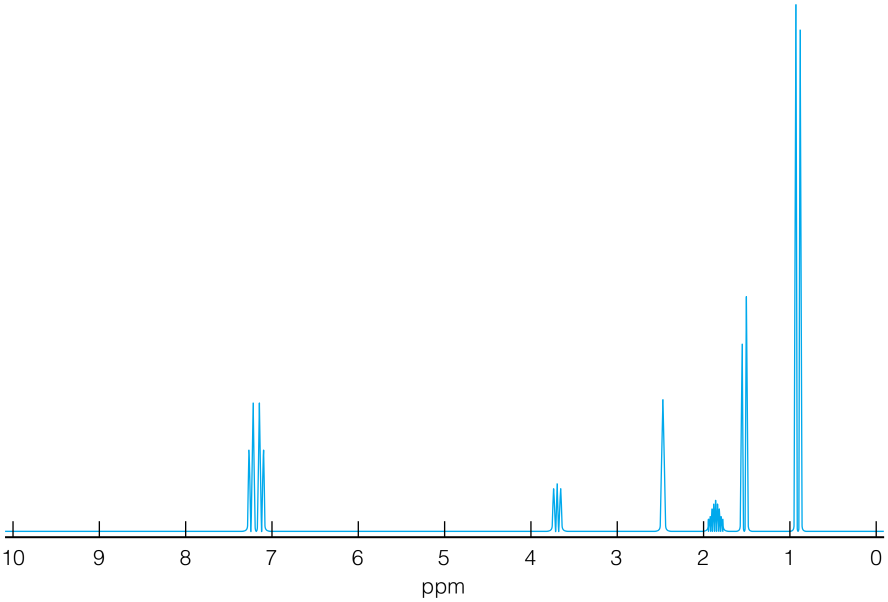

Figure 16.18 A high-resolution spectrum shows the effects of spin-spin coupling, mostly between hydrogens on adjacent atoms in a molecule. *Source:* S. E. Sen and K. S. Aniker, *J. Chem. Ed.,* 1996, 74: 570.

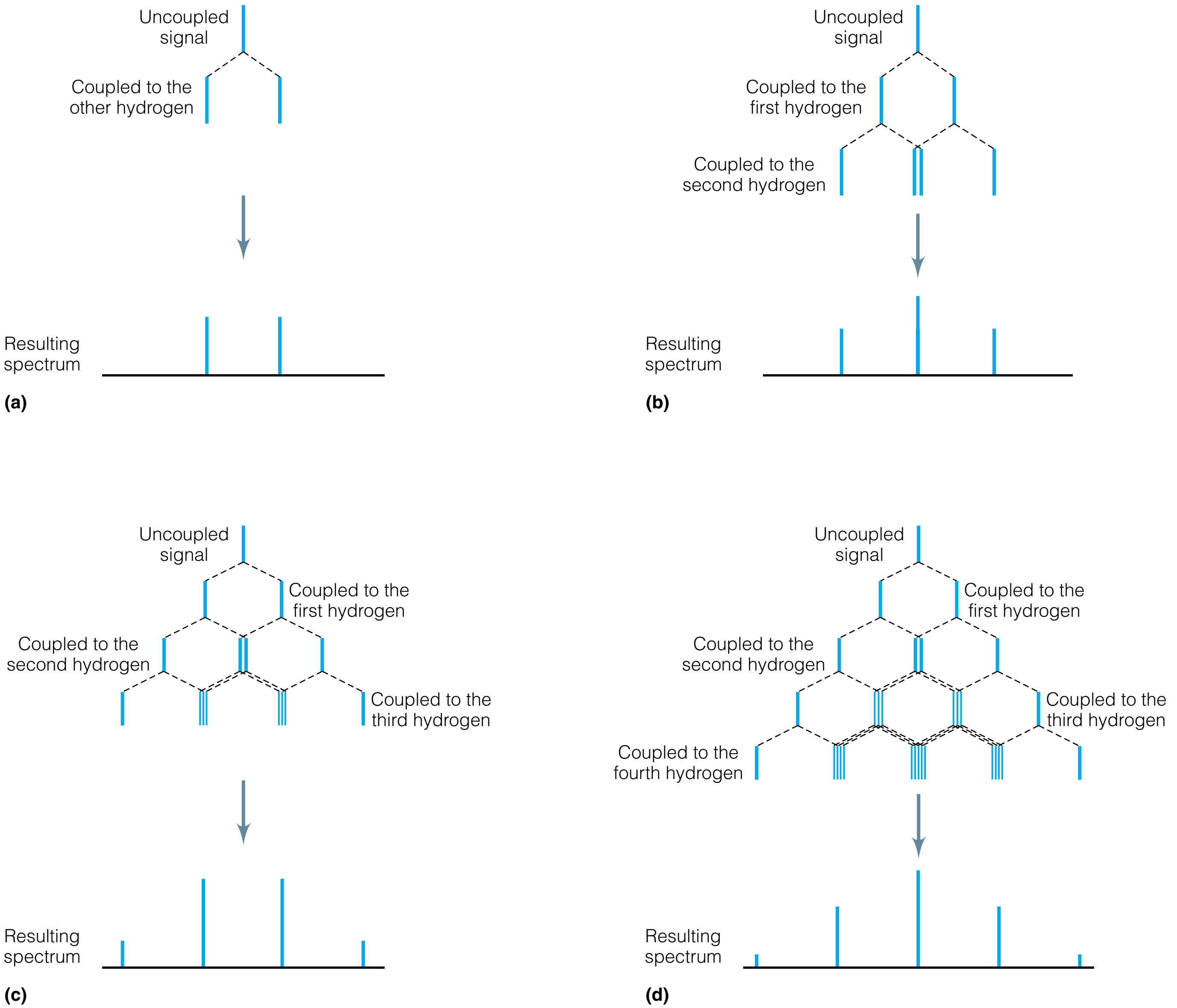

Figure 16.19 The nuclei of *n* hydrogens on adjacent atoms of C or O in a molecule couple with the proton NMR signal and split the absorption into $n + 1$ peaks. These peaks have characteristic intensity ratios, as illustrated for a hydrogen having (a) 1, (b) 2, (c) 3, and (d) 4 neighbors.

hydrogen atoms, and ultimately only the hydrogen atoms bonded to *adjacent* carbon atoms will participate in spin-spin coupling. (Hydrogens that are attached to the same carbon do couple, but selection rules are such that transitions to such coupled states are not observed. Therefore, the only coupling that is observed occurs between hydrogens on *different* carbons.) For nuclei having spin $I = \frac{1}{2}$ (which includes ^{1}H and ^{13}C, the two most prevalent nuclei studied by NMR), the presence of *n* nuclei induces a splitting of an absorption into $n + 1$ individual absorptions. This splitting occurs whether the nuclei on adjacent carbons are equivalent or not.

The split NMR peaks also have a characteristic intensity pattern. A double peak consists of two peaks of roughly equal intensities. Three peaks have intensity ratios of roughly 1 : 2 : 1. A quartet has intensities of roughly 1 : 3 : 3 : 1, and so forth. The relative intensity patterns are caused by the overlapping of absorptions that are split by spin-spin coupling, as illustrated in Figure 16.19.

1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1
1 6 15 20 15 6 1
. . .

Figure 16.20 Pascal's triangle, a mnemonic for remembering the coefficients on the polynomial expansion $(x + 1)^n$. These numbers are called binomial coefficients, and are also applicable to the intensities of split NMR signals.

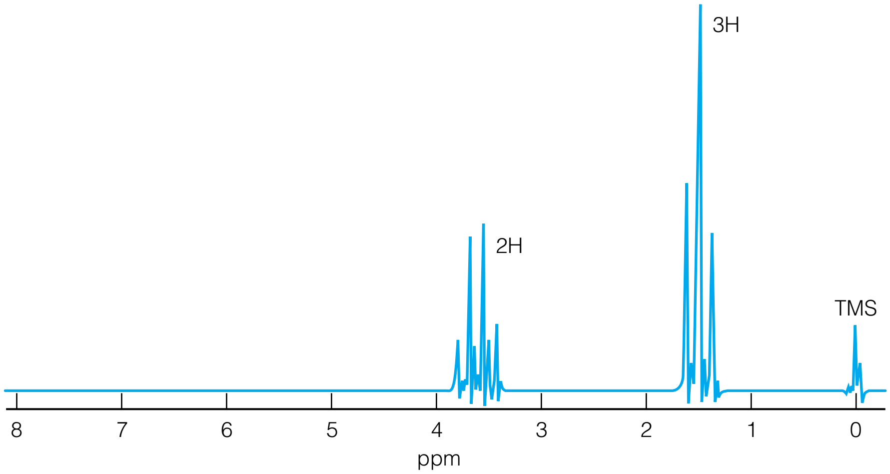

Figure 16.21 At higher resolution, the NMR spectrum in Figure 16.17 shows the splitting of the proton absorptions, with intensity ratios as predicted.

These relative intensity ratios are familiar. They are, indeed, the binomial coefficients, which are the coefficients of the polynomial expansion $(x + 1)^n$, where $n = 0, 1, 2, 3, \ldots$. These coefficients are shown in Figure 16.20 in their most familiar form, called Pascal's triangle (named after the seventeenth-century French mathematician Blaise Pascal). Furthermore, the integrated intensity of each set of absorptions is directly proportional to the number of hydrogens having that specific chemical environment. Figure 16.21 shows the same NMR spectra as in Figure 16.17, but at higher resolution. More information is available from the high-resolution spectra, which have become the standard.

Example 16.12

Describe the high-resolution spectrum of each of the following:

a. Methane, CH_4
b. Ethane, CH_3CH_3
c. Propane, $CH_3CH_2CH_3$

Solution

a. Methane has four hydrogens on one carbon atom. Since the selection rules do not allow one to observe the coupling between hydrogens on the same carbon, there will be only a single NMR absorption even in the high-resolution spectrum.

b. Ethane has six hydrogens in the same chemical environment, but the coupling between the hydrogens splits the single low-resolution spectrum into $n + 1 = 3 + 1 = 4$ individual lines. This splitting into what is called a quartet of lines is exactly the same for both CH_3 groups, so one observes only a single quartet of absorptions, with intensity ratios of roughly 1 : 3 : 3 : 1, in the NMR spectrum.

c. There are two different chemical environments in propane. The hydrogens in each CH_3 group couple to the two hydrogens in the CH_2 group in the same way, so the methyl hydrogens are split into three individual peaks (a triplet) with intensity ratios of 1 : 2 : 1. The CH_2 protons are also coupling with all of the hydrogens in the methyl groups, so the absorption from those hydrogens

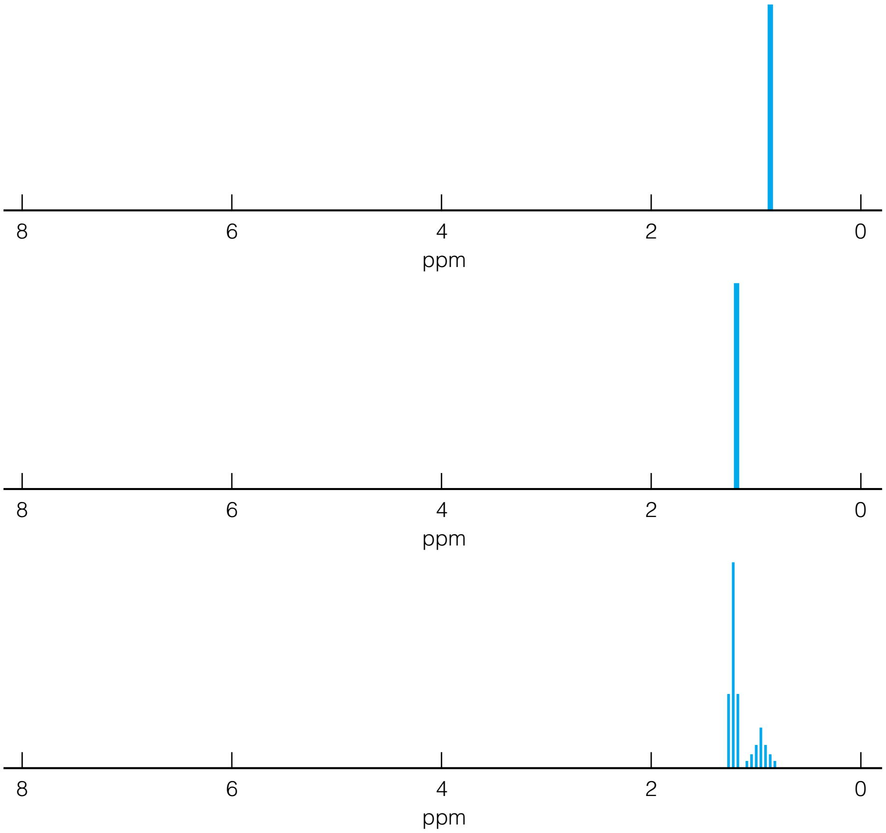

Figure 16.22 High-resolution NMR spectra of methane, ethane, and propane show the splittings of the proton absorbances, as expected by the number of neighboring hydrogen atoms on each carbon.

splits into a total of 6 + 1 = 7 individual absorptions (a heptet). The relative intensities of the triplet/heptet absorptions should be in the ratio of 6 : 2 (or 3 : 1), which is the ratio of the number of environmentally equivalent hydrogens in the molecule. Figure 16.22 shows NMR spectra of the three compounds.

Just like IR spectra for vibrational motions of molecules, the chemical shifts seen in NMR spectra are generally characteristic of the type of groups in a molecule. That is, methyl groups typically show up in an NMR spectrum shifted about 1 ppm away from TMS, hydrogens on aromatic rings typically show up about 7–8 ppm away from TMS, and so on. General ranges of positions due to specific groups are gathered in correlation charts (just like IR spectroscopy). An example of an NMR correlation chart for proton NMR is shown in Figure 16.23.

Modern NMR spectrometers have the capability of measuring the resonance absorption of multiple nuclei, like ^{1}H, ^{13}C, ^{31}P, and other elements. Modern instruments don't typically use a straight absorption-of-electromagnetic-radiation mode of measuring a spectrum. Instead, the spectrometer exposes the nuclei to a static magnetic field, B_0, which aligns the magnetic moments of the nuclei. Then, a second magnetic field B_1 that is perpendicular to B_0 is applied to the sample for a short time (1–10 microseconds), as a pulse.

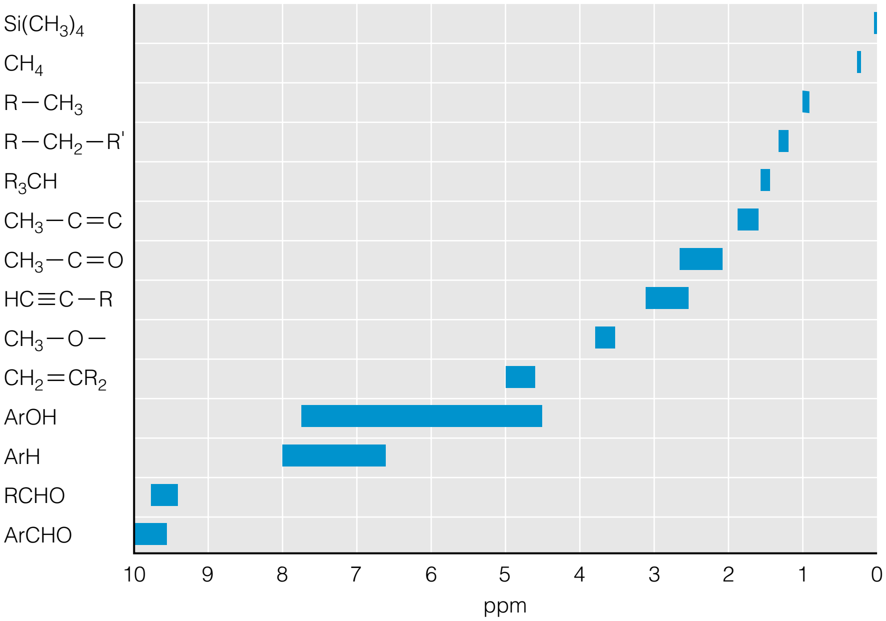

Figure 16.23 NMR correlation chart, showing where different types of hydrogens attached to different atoms absorb in an NMR spectrum.

This perpendicular pulse causes the magnetic moments of the nuclei to precess in a circular path, an effect that can be measured by a detector coil around the sample. As soon as the pulse stops, the precession decreases as nuclei realign with the static B_0 magnetic field. This process is called *relaxation*, and has several mechanisms that we won't discuss but that are related to the identity of the sample. A plot of the signal measured by the detector versus time is called *free induction decay* (FID).

A mathematical function called a Fourier transform (FT) is applied to the FID signal, which converts it into an NMR spectrum. The advantages of such pulse techniques include the ability to store data digitally in a computer, which can record multiple spectra and average them together. In this way, noise is reduced and a clearer spectrum is possible. In fact, some NMR spectra are so noisy that magnetic resonance spectra are illegible when performed in a scanning mode, so they must be performed in a pulsed mode. ^{13}C spectra are one example. An FT-NMR ^{13}C spectrum is shown in Figure 16.24.

NMR has aspects not discussed here that make it one of the most powerful techniques for studying the structures of molecules that have NMR-active

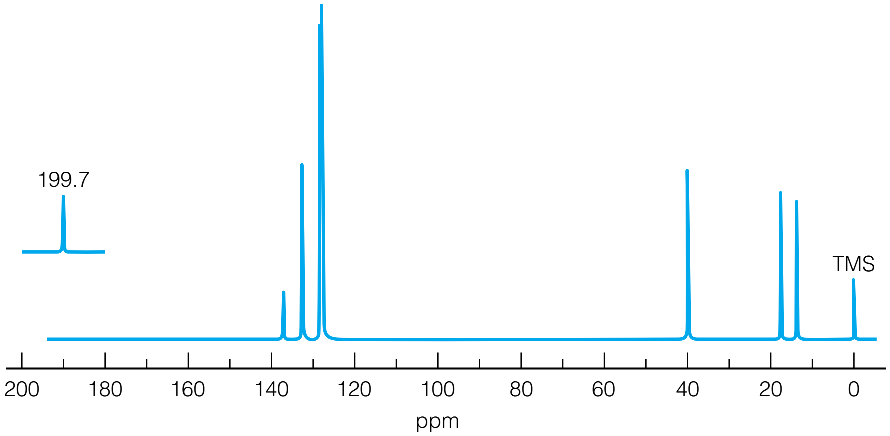

Figure 16.24 ^{13}C NMR spectrum of phenyl propyl ketone, $C_6H_5COC_3H_7$.

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Figure 16.25 NMR is used in the medical field to generate pictures of the inside of the body for diagnostic purposes. In medical terminology, it is called magnetic resonance imaging.

nuclei. Many of these aspects are ultimately based on the physical interactions discussed in this chapter.

NMR has found some use in the medical field (see Figure 16.25), where large nuclear magnetic resonance spectrometers are set up so that people can be used as samples. A patient is placed in a magnetic field and bombarded with harmless radio waves. NMR signals from the protons in the tissues can be analyzed. In this way, the status of the bodily tissues can be determined, and with the computer control that is available, medical doctors can obtain many perspectives of the tissues inside a patient without any sort of invasive procedures. Problems like tumors, spinal irregularities, and cardiovascular disease can be evaluated without harm to the patient. However, in the medical field the technique is referred to as *magnetic resonance imaging,* or MRI. Apparently the word “nuclear” is dropped because of its connotations. Be that as it may, MRI is still NMR, a *nuclear* spin phenomenon.

16.6 Summary

Besides those presented here, other types of spectroscopy use magnetic fields to help differentiate among the wavefunctions of molecules. The three types discussed here—Zeeman, ESR, and NMR—only scratch the surface. Magnetic spectroscopy is useful in chemistry in part because of its ability to access individual wavefunctions that are normally degenerate. An even closer look, with the appropriate amount of group theory thrown in, would show that magnetic spectroscopic techniques can determine a lot about atomic and molecular systems. Because of how the electrons and nuclei interact with each other, we can derive specific structural information about molecules. Such information, when combined with information from other sources like vibrational or rotational or electronic spectroscopy, helps give us a perfect picture of what atoms and molecules look like. All this is based on the theory of quantum mechanics, the explanation for how subatomic particles behave. All of spectroscopy is a testament to the fact that quantum mechanics works and can give us information about the world around us.

16.2 Magnetic Fields and Dipoles, and Electric Charges

16.1. What is the difference between a magnetic field vector and a magnetic dipole vector?

16.2. Assuming that you are surrounded by six electrical wires right now, each 2.00 meters away and that each one is carrying 10 amps of charge in the same direction, what magnetic field are you exposed to?

16.3. (a) If the electron were to have a positive charge, what would be the difference in the magnitude calculated in Example 16.2b for the magnetic dipole caused by an electron in the hydrogen atom?

(b) *Positronium* is very similar to a hydrogen atom except that instead of a proton in the nucleus, there is a positron. (This short-lived "element" can be made in the laboratory.) On the basis of your answer to part a, what is the overall magnetic dipole caused by the two particles in mutual orbit about each other?

16.4. Show that 1 tesla is equal to 1 $J/(m^2 \cdot amp)$.

16.5. Verify the value and units of the Bohr magneton, μ_B.

16.3 Zeeman Spectroscopy

16.6. Draw and label the allowed electronic transitions for a $^1S \rightarrow {}^1P$ transition with and without a magnetic field. How do the total number of allowed transitions differ?

16.7. (a) For the above $^1S \rightarrow {}^1P$ transition, calculate ΔE in the transition energies for each individual transition when a sample is exposed to a magnetic field of 2.35 T. **(b)** Repeat the calculation, but now for a $^1P \rightarrow {}^1D$ transition.

16.8. What magnetic field is needed to obtain a ΔE value of 1.0 cm^{-1} between the highest and lowest levels of a ^1F state?

16.9. Calculate the maximum splitting of the $^2P_{3/2}$ state of the hydrogen atom due to Earth's magnetic field, which you can take as having a value of 0.6 gauss.

16.10. How many **(a)** individual transitions and **(b)** unique spectral lines (that is, lines having a different energy) are allowed for a $^1D \rightarrow {}^1P$ transition? (See exercise 16.7b.)

16.11. Calculate the Landé g factor for a $^5D_4$ state of the Fe atom using both equations 16.12 and 16.13 and determine the deviation introduced by approximating $g_e \approx 1$.

16.12. (a) Calculate the ΔE values experienced by the ground-state energy levels when an atom of V is exposed to a magnetic field of 5.57×10^3 G. Vanadium has an $^4F_{3/2}$ ground state.

16.4 ESR Spectroscopy

16.13. What are the energies in J/photon for the microwave radiation frequencies used in ESR spectroscopy?

16.14. What magnetic field strengths are necessary to achieve resonance for each of the microwave frequencies used in ESR spectroscopy?

16.15. How many ESR signals would be expected from the amine radical, $NH_2\cdot$?

16.16. How many ESR signals would be expected from the cyclopentadienyl radical, $C_5H_5\cdot$?

16.17. How many ESR signals would be expected from the cycloheptatrienyl radical, $C_7H_7\cdot$?

16.18. What magnetic field strength is necessary to achieve resonance between the two spin states of an electron on a compound where the difference in the energy levels is 7.204×10^{-24} J? Assume a g_e value of 2.0023.

16.19. What is the wavenumber of the microwave radiation absorbed by an unpaired electron in a magnetic field of 3476 gauss that has a g_e value of 2.0058?

16.20. Nitrogen makes oxide compounds of varying stoichiometry, including NO, NO_2, N_2O_4, and N_2O_5. Predict which of these molecules will be ESR-active in their un-ionized, molecular form.

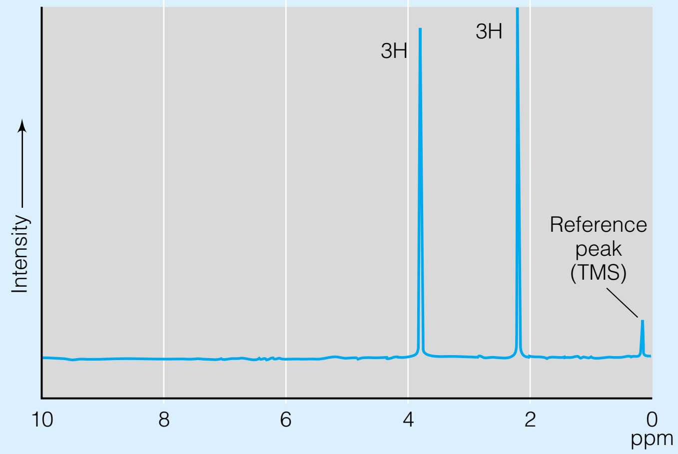
16.21. An ESR spectrum of an unknown radical is split into six lines. Which of the following atoms could be in the radical? **(a)** ^{42}K **(b)** ^{35}Cl **(c)** ^{37}Cl **(d)** ^{67}Zn **(e)** ^{47}Ti **(f)** ^{32}S (*Hint:* A table of nuclear spins is necessary to answer this question. Such a table is in Appendix 5 of this text.

16.22. The hyperfine coupling constant a for deuterium, D (which is ^2H), is 78 gauss. Predict the ESR spectrum of the ND_2 radical at a magnetic field of 3482 gauss.

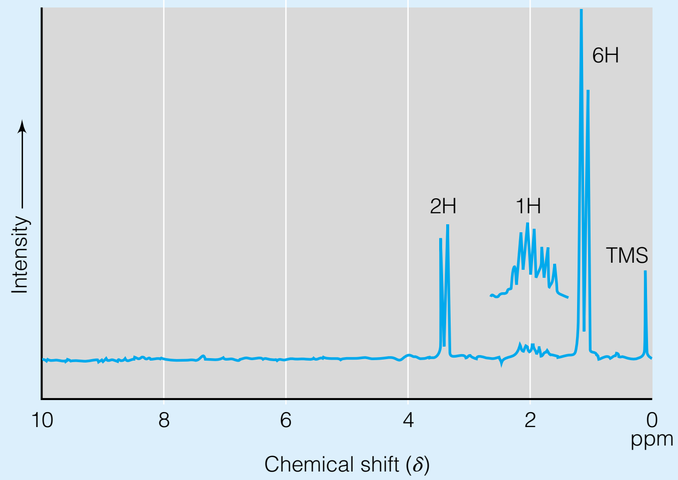
16.5 NMR Spectroscopy

16.23. Do the NMR transitions from $M_I = -\frac{1}{2}$ to $M_I = +\frac{1}{2}$ appear at the same wavelengths or different wavelengths from the $M_I = +\frac{1}{2}$ to $M_I = +\frac{3}{2}$ transition of the same nucleus? Justify your answer mathematically.

16.24. Which of the following nuclei will have an NMR spectrum? **(a)** ^2H **(b)** ^{14}C **(c)** ^{16}O **(d)** ^{19}F **(e)** ^{28}Si **(f)** ^{31}P **(g)** ^{55}Mn **(h)** ^{238}U (*Hint:* Again, a table of nuclear spins is necessary for this question. See Appendix 5 for the data you need.)



(a) $C_3H_6O_2$



(b) C_4H_9Br

Figure 16.26 NMR spectra.

16.25. Calculate the strength of the magnetic field necessary to observe NMR signals of the NMR-active nuclei from exercise 16.24 using a spectrometer that generates radiation having a frequency of 330 MHz.

16.26. Describe the effect of spin-spin coupling on the proton NMR absorptions of **(a)** butane, **(b)** cyclobutane, and **(c)** isobutane (2-methylpropane). How would you tell these compounds apart by their NMR spectra?

16.27. Use the NMR spectra and molecular formulas in Figure 16.26 to determine tentative identifications of the compounds. Assume the compounds are pure. Use the NMR correlation chart (Figure 16.23) to assist your identification.

16.28. Calculate the changes in the nuclear energy levels of a ^{35}Cl nucleus ($I = \frac{3}{2}$) exposed to a magnetic field of 3.45 T. The g_N value for ^{35}Cl is 0.5479.

16.29. Calculate the ΔE values of the allowed transitions for a ^{35}Cl nucleus ($I = \frac{3}{2}$) exposed to a magnetic field of 3.45 T. The g_N value for ^{35}Cl is 0.5479. Express the answers in MHz.

16.30. Although boron atoms have a nonzero nuclear spin, boron NMR is more complicated than proton NMR or ^{13}C NMR. Why?

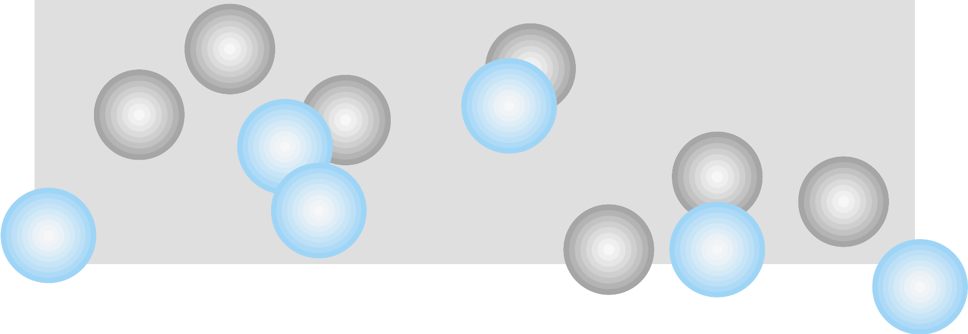
16.31. A microwave oven emits radiation having a frequency of 2.45 GHz. What magnetic field is necessary to see NMR transitions of ^{119}Sn, which has a spin of $\frac{1}{2}$ and a g_N value of 2.0823?

Symbolic Math Exercises

16.32. Make a table of Landé g factors for L, S, and J having values of up to 4. Comment on the effect of the various g factors on the magnitude spectra of atoms.

17

Statistical Thermodynamics: Introduction



THERMODYNAMICS IS ONE OF THE FEW TOPICS that one can approach from two completely different perspectives and arrive at the same answers. One approach, the *phenomenological approach*, is the subject of the first eight chapters of this book. It is based on the observation of *phenomena*, whose behaviors are generalized by various algebraic and calculus expressions. Over the course of hundreds of thousands of observations, some generalities have been used as summaries to describe how all known systems should behave. These summaries are known as the three laws of thermodynamics.

There is another way to consider thermodynamic properties: a *statistical approach*. Years before the quantum theory of matter was formulated, the atomic theory was becoming the cornerstone of chemistry. Some people—James Clerk Maxwell, Ludwig Boltzmann, and J. Willard Gibbs among them—thought that if atoms and molecules were so small, then perhaps their behavior with respect to energy could be understood statistically. Many of their scientific contemporaries rejected the idea. (In fact, Boltzmann's suicide is blamed partly on the negative reception given his ideas.) However, it turns out that we *can* use statistics to understand the thermodynamics of atoms and molecules. Ultimately, we find that the statistical approach allows us to make the same thermodynamic predictions as with the phenomenological approach. This new approach is called *statistical thermodynamics*.

17.1 Synopsis

We will begin with a necessary (but nonchemical) review of some statistics that we later apply to gaseous systems. (We use gases almost exclusively in our discussion of statistical thermodynamics.) We will see how we can separate, or partition, a system into smaller units and define an important quantity called a partition function. In time, we will see that the partition function is related to the thermodynamic state functions that define our system.

The partition function is defined in terms of the different possible energies of the individual particles in a system. The developers of statistical thermodynamics derived their equations without an understanding of the quantum theory of nature. But now, we recognize that atomic and molecular behavior is described by quantum mechanics, and our development of statistical thermodynamics must recognize that. It is why we have put off a discussion of statistical thermodynamics until after our treatment of quantum mechanics.

In this chapter, we will develop the tools and apply them to atomic systems. The monatomic inert gases (He, Ne, Ar, Kr, Xe) will serve as our examples. The next chapter will deal with diatomic and larger molecules.

17.2 Some Statistics Necessities

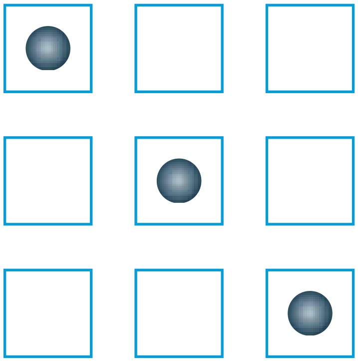


Figure 17.1 There are only three ways of putting a single ball in three identical boxes.

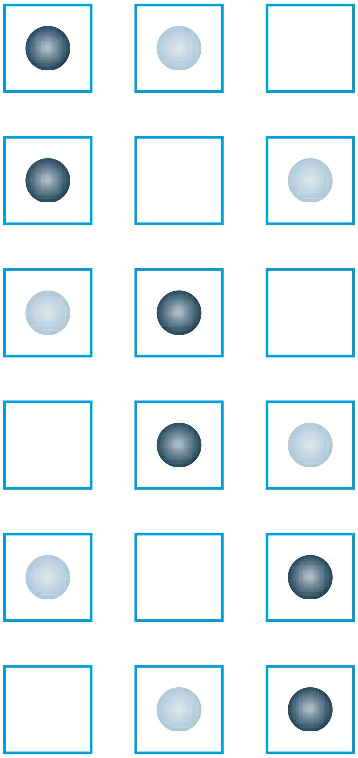


Figure 17.2 If two different balls are placed in three identical boxes, it turns out that there are now six possibilities. Compare this with the situation where the balls are identical: in that case only three distributions are possible among the three boxes. This illustrates the difference in number of possible arrangements for distinguishable versus indistinguishable objects.

In order to understand statistical thermodynamics, it is necessary to review some statistical ideas. For example, consider a system that is composed of three boxes that represent smaller subsystems. How many ways are there of putting a single black ball into the three identical but separate boxes? There are three ways, as shown in Figure 17.1. How many ways are there of putting two identical black balls in the three identical boxes, one ball per box? Again, only three. (Verify this.)

How many ways are there to distribute a black ball and a white ball in the three identical boxes? There are six ways. The six possibilities are shown in Figure 17.2. Because the balls are different, the possible arrangements for our distributions are different than if the balls were identical.

The two different systems of same- and different-colored balls illustrate the concepts of *distinguishable* versus *indistinguishable* objects. When the objects that are being partitioned into separate subsystems are distinguishable, there are more possible ways of arranging the objects in the subsystems. However, if the objects are indistinguishable, there are fewer unique ways.

In considering the arrangements in Figures 17.1 and 17.2, it is common to express the population of the subsystems (here, the boxes) in terms of probabilities. In Figure 17.1, for example, in one of three total cases the ball is in the first box. Therefore, if we are considering all possible arrangements, we might wonder what the probability is that if any specific arrangement were selected at random a ball would be in the first box. Since one out of three arrangements satisfies this criterion, we can say that the probability of finding a ball in the first box is one out of three, which we can express as $\frac{1}{3}$ or 33%. Probabilities are often expressed as percentages.

Example 17.1

Referring to Figure 17.2, what is the probability of finding the following?

a. Any ball in the second box

b. A white ball in the third box

Solution

a. Figure 17.2 has four arrangements out of the six that have a ball in the second box. Therefore, the probability of finding a ball in the second box is $\frac{4}{6}$, or 67%.

b. If we specify that the ball in the third box must be a white ball, then only two arrangements out of the six satisfy this criterion. This probability is therefore $\frac{2}{6}$, or 33%.

The number of possible unique groupings of distinguishable objects into various subsystems is determined by the combination formula. If there are m subsystems in the system and N objects, and there are n_1 objects in subsystem 1,

n_2 objects in subsystem 2, and n_i objects in the ith subsystem, then the number of ways of accomplishing this arrangement, labeled C, is given by the *combination formula*

$$C = \frac{N!}{\prod_{i=1}^{m} n_i!} \tag{17.1}$$

where $N!$ is "N factorial" or $1 \cdot 2 \cdot 3 \cdot 4 \cdot \cdot \cdot \cdot N$ and the $\Pi n_i!$ in the denominator is the product of all of the n_i values. The n_i values are called *occupation numbers*. By definition, $0! = 1$ and $1! = 1$.

In our future consideration of atomic and molecular systems, the number of subsystems N and the occupation numbers will be very large. We would then have to evaluate $N!$ where N is a very large number, on the order of Avogadro's number. However, it is easily shown on a calculator that $N!$ gets very large, very fast. (A point of calculator trivia is that 69! is just under 10^{100}, which is the largest factorial that many calculators can evaluate.) We will need to find some way of evaluating factorials of very large numbers.

There is a method of estimating the *natural logarithm* of factorials. *Stirling's approximation* says that, for large N,

$$\ln N! \approx N \ln N - N \tag{17.2}$$

This approximation will be useful when we apply combination statistics to collections of molecules. To give you an example of how well it works, consider the following table:

N	$\ln N!$	$N \ln N - N$	% error
30	74.66	72.04	3.51
100	363.74	360.52	0.885
5000	37,591	37,586	0.0133

Notice that the percentage error between $\ln N!$ and $N \ln N - N$ goes down as N increases. Stirling's approximation gets better as N increases, so it will be very useful in considering macroscopic systems of moles of atoms and molecules.

Probabilities can also be used to determine average values of some variable. Consider a variable u that can have certain possible individual values u_j. Further, we will represent the probability that any particular value u_j exists as P_j. The average value of the variable u, which we designate $\bar{u}$, is given by the expression

$$\bar{u} = \frac{\sum_{j=1}^{\text{possible values}} u_j \cdot P_j}{\sum_j P_j} \tag{17.3}$$

We can illustrate the correctness of this equation with a simple example. A class of seven students is given a quiz worth up to 10 points. The individual scores are 7, 9, 9, 4, 2, 10, and 8. What is the average score on the quiz? One way to determine an average is to add the individual scores, then divide by the number of scores:

$$\overline{\text{score}} = \frac{7 + 9 + 9 + 4 + 2 + 10 + 8}{7} = \frac{49}{7} = 7$$

But we can also use equation 17.3 if we first determine the probabilities of each score in the grades. Since the score of 0 does not appear in the list of individual scores, we say that $P_0 = \frac{0}{7}$. A score of 1 does not appear either, so $P_1 = \frac{0}{7}$ also. But one score of 2 does appear once out of seven grades, so we can say that $P_2 = \frac{1}{7}$. Similarly, we have $P_3 = \frac{0}{7}$, $P_4 = \frac{1}{7}$, $P_5 = \frac{0}{7}$, $P_6 = \frac{0}{7}$, $P_7 = \frac{1}{7}$, $P_8 = \frac{1}{7}$, $P_9 = \frac{2}{7}$ (there are two 9's), and $P_{10} = \frac{1}{7}$. (You should verify all these probabilities.) The individual score (out of 10) is represented by u_j, so by equation 17.3 we have for the average score

$$\overline{\text{score}} = \frac{\sum_{j=1}^{10} u_j \cdot P_j}{\sum_j P_j}$$

$$= \frac{0 \cdot \frac{0}{7} + 1 \cdot \frac{0}{7} + 2 \cdot \frac{1}{7} + 3 \cdot \frac{0}{7} + 4 \cdot \frac{1}{7} + 5 \cdot \frac{0}{7} + 6 \cdot \frac{0}{7} + 7 \cdot \frac{1}{7} + 8 \cdot \frac{1}{7} + 9 \cdot \frac{2}{7} + 10 \cdot \frac{1}{7}}{\frac{0}{7} + \frac{0}{7} + \frac{1}{7} + \frac{0}{7} + \frac{1}{7} + \frac{0}{7} + \frac{0}{7} + \frac{1}{7} + \frac{1}{7} + \frac{2}{7} + \frac{1}{7}}$$

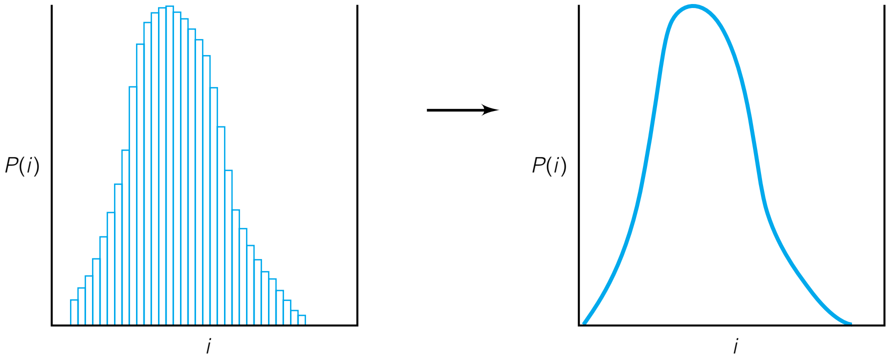
$$= \frac{0 + 0 + \frac{2}{7} + 0 + \frac{4}{7} + 0 + 0 + \frac{7}{7} + \frac{8}{7} + \frac{18}{7} + \frac{10}{7}}{\frac{7}{7}}$$

$$= \frac{\frac{49}{7}}{1} = \frac{7}{1} = 7$$

We get the same answer for the average score. Although for this example the probability method is more cumbersome, for large numbers of values (here, "scores") it will become easier than the simple averaging method.

For a small number of possible arrangements, it is easy to determine the total number of possibilities by counting them. For example, if Figure 17.3a represents the possibilities for various arrangements of a system, the total number of possible arrangements is determined by adding the individual values represented by the bars in the graph. However, as the number of possibilities increases, it becomes progressively more time-consuming, and ultimately impossible, to determine the total number of possibilities by adding the discrete number of arrangements.

However, if the distribution of probabilities can be expressed by a smooth function as in Figure 17.3b, then the total number of possible arrangements—equal to the area under the curve—is given by the integral of that probability



(a) No. of possibilities = $\Sigma P(i) \times i$ **(b)** No. of possibilities = $\int P(i)\, di$

Figure 17.3 For a smooth distribution, an integral can be substituted for a summation. This allows us to use calculus in our derivation of expressions in statistical thermodynamics.

function over all possible arrangements. For balls in boxes, summing the probabilities is easily done. But for gaseous systems, in which the number of particles can be on the order of 10^{20}, we will favor the approach of integrating a smooth function. This perspective implies that the mathematics of calculus will be useful to us in understanding the statistical behavior of our system.

17.3 The Ensemble

One of the ways that statistical thermodynamics tries to understand the thermodynamic state of a large *macroscopic* system is by separating it into tiny, or *microscopic,* parts. These parts are called *microsystems.* The state of each microsystem is called the *microstate.* Understand that each microsystem may have a different individual microstate, including volume, pressure, temperature, energy, density, and so on. All of the microstates of the system combine statistically to generate the overall state, or *macrostate,* of the system: its overall temperature, pressure, volume, energy, and so on. This is a basic postulate of statistical thermodynamics. In order to understand how these microstates combine, we will first have to separate our system into microsystems and determine the microstates of the microsystems.

There are several ways to do this. A convenient way will be chosen for our purposes. We define the term *ensemble* as a collection of an undetermined number of microsystems that collectively make up our macroscopic system. Figure 17.4 illustrates one way of mentally separating a macroscopic system into an ensemble of microsystems. Each microsystem in the ensemble has its own characteristic microstate, defined by a particular number of particles, energy, volume, pressure, temperature, and so on. It is common to use the terms “microsystem” and “microstate” interchangeably, although technically the microstate is the set of conditions that define the state of the microsystem.

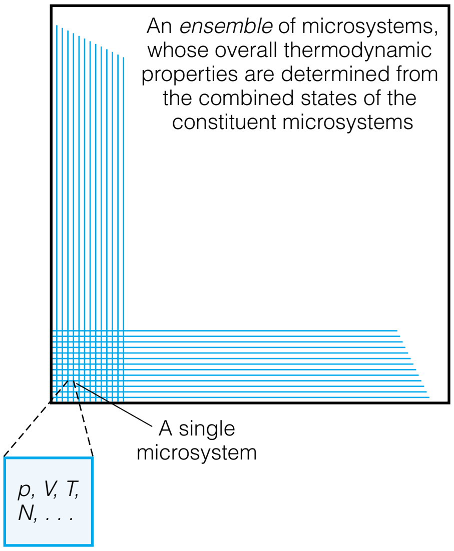


Figure 17.4 This is one hypothetical way of dividing a large system into an ensemble of smaller microsystems. The individual states of the microsystems combine to determine the overall state of the system.

A *canonical ensemble* is an ensemble separated into j individual microstates such that the numbers of particles in each microstate N_j, the volumes of the microstates V_j, and the temperatures of the microstates T_j are the same.* As extensive variables, particle numbers and the volumes are additive over the microstates, whereas the temperature, an intensive variable, is *not* additive over the ensemble. Another way of saying this is by defining the total number of particles N, the system’s total volume V, and the system’s overall temperature T as

$$N = \sum_j N_j = j \cdot N_j \qquad \textbf{(17.4)}$$

$$V = \sum_j V_j = j \cdot V_j \qquad \textbf{(17.5)}$$

$$T = T_j \qquad \textbf{(17.6)}$$

Consider the energy of the particles in an ensemble. From quantum mechanics, we recognize that energy can have only certain values for the elec-

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*There are other ways to define ensembles. For example, a *microcanonical ensemble* is defined as a set of microstates in which the volume, number of particles, and energies of each microstate are the same. So although equations 17.4 and 17.5 are still valid for a microcanonical ensemble, equation 17.6 is not. Rather, for a microcanonical ensemble we have

$$E_{\text{system}} = \sum_j E_j = j \cdot E_j$$

Grand canonical ensembles have V, T, and μ (chemical potential) the same for all microsystems.

tronic, translational, rotational, vibrational, and other quantum states. We will denote the energy level of the gas particle as ϵ_j: ϵ_0 is the ground (that is, minimum-energy) state, ϵ_1 is the first excited state, ϵ_2 is the second excited state, and so on. If we are going to understand the thermodynamics of the macrostate, we will need to keep track of how many gas particles have which energy in which microstate.

If we assume that N_0 gas particles are in the energy state ϵ_0, N_1 particles are in energy state ϵ_1, N_2 particles are in energy state ϵ_2, and so on, then how many ways can the particles be distributed with this total energy? This is a combination type of problem, just like putting balls into boxes. If we denote the number of ways we can make this arrangement as W, then by applying equation 17.1, we have

$$W = \frac{N!}{N_1! \cdot N_2! \cdot N_3! \cdot \cdots} \tag{17.7}$$

This is just the number of ways of arranging the right number of particles in the specified energy states. If we consider the degeneracy of each energy state, g_j, then the total number of possible ways must include the degeneracies as a factor. If there are N_j particles with degeneracy g_j, then the number of ways the N_j particles can be arranged among these degenerate states is $(g_j)^{N_j}$. [For example, having two particles with doubly degenerate wavefunctions allows for four possible ways (2^2) the particles can have particular wavefunctions.] For all particles and all degeneracies, the total number of arrangements due to degeneracies is the product of the individual degeneracies:

$$W_{\text{deg}} = (g_0)^{N_0} \cdot (g_1)^{N_1} \cdot (g_2)^{N_2} \cdot (g_3)^{N_3} \cdot \cdots = \prod_j (g_j^{N_j}) \tag{17.8}$$

in which the degeneracy of the ground state, g_0, is taken N_0 times (for the N_0 particles that have energy ϵ_0), and so on. Keep in mind that degeneracies can be very large; for translational states of a mole of atoms, the degeneracy is on the order of 10^{20}. The total number of ways these N particles might exist in that arrangement, denoted Ω, is the product of W and W_{deg}:

$$\Omega = W \cdot W_{\text{deg}} = \frac{N!}{\prod_j N_j!} \cdot \prod_j g_j^{N_j} \tag{17.9}$$

N_0, N_1, N_2, etc., are the occupation numbers for each particular energy level. As you might expect, Ω is a *huge* number. Additionally, we have assumed a specific set of occupation numbers N_j. Can the system have some other set of N_j values? Of course it can. One of the questions of statistical thermodynamics is whether it can predict *which* set of occupation numbers is most probable.

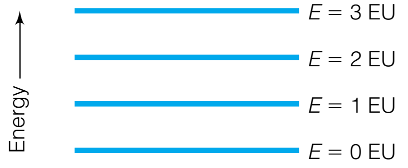


Figure 17.5 Refer to Example 17.2. How many ways are there of distributing three distinguishable particles so that there are 5 energy units in the system?

Example 17.2

Assume that you have a three-particle system that has four possible energy states, as shown in Figure 17.5. Your system has a total of 5 energy units (5 EU's) to distribute among the particles. How many different distinguishable distributions can there be? Can you use the occupation numbers to verify equation 17.7?

Solution

Refer to Figure 17.6. Each drawing shows a way to distribute the particles in the possible quantum states so that the complete system has 5 EU's. Under

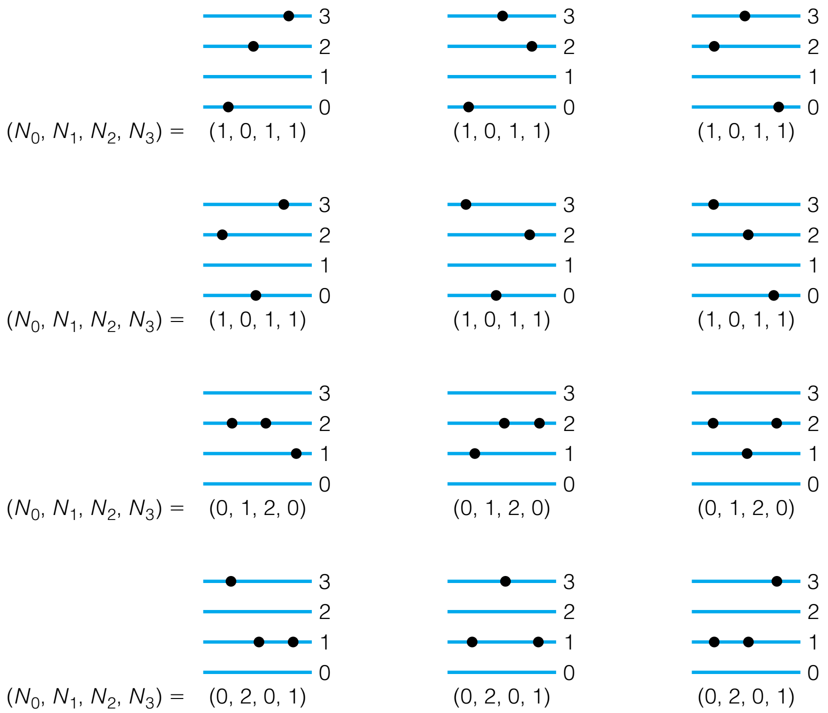


Figure 17.6 Refer to Example 17.2. These are the only ways of distributing the three particles (shown as a left, a middle, and a right dot) to get 5 energy units in the system. Notice that there are six possible combinations of the occupation number set (1, 0, 1, 1) but only three possible combinations of the occupation number sets (0, 1, 2, 0) and (0, 2, 0, 1).

each drawing, the occupation numbers N_0, N_1, N_2, and N_3 are listed. By applying equation 17.7, we can see that

$$W(1, 0, 1, 1) = \frac{3!}{1! \cdot 0! \cdot 1! \cdot 1!} = 6$$

$$W(0, 1, 2, 0) = \frac{3!}{0! \cdot 1! \cdot 2! \cdot 0!} = 3$$

$$W(0, 2, 0, 1) = \frac{3!}{0! \cdot 2! \cdot 0! \cdot 1!} = 3$$

Figure 17.6 shows that there are 6, 3, and 3 ways of distributing the particles among the possible energy levels so that the total energy equals 5.

Referring to Example 17.2, we see that there are 12 possible arrangements of the particles in three distinct ways, each of which has multiple possibilities. Which of these 12 ways is preferred? Putting the question another way, if we have an ensemble of microstates for a system that has 5 energy units, which of the arrangements in Figure 17.6 will be favored? Statistical thermodynamics assumes that none of the arrangements is preferred over the others, that all possible arrangements are equally probable. This is known as the *principle of equal a priori probabilities.*

Does this mean that each set of occupation numbers (1, 0, 1, 1), (0, 1, 2, 0), and (0, 2, 0, 1) will make up a third of the overall system? No, it doesn't, because there are six ways of making the occupation numbers (1, 0, 1, 1) and only three ways each of making (0, 1, 2, 0) and (0, 2, 0, 1). It does mean that $\frac{1}{12}$ of the system will be represented by each drawing in Figure 17.6. Because there are more ways of making a system with the occupation numbers (1, 0, 1, 1), there will be more microstates having that arrangement. This idea becomes very important when considering large numbers of gas particles that exist in any real system.

17.4 The Most Probable Distribution: Maxwell-Boltzmann Distribution

Let us now consider a canonical ensemble that describes an isolated system in which N_j, V_j, and T are the same for all microstates. The energies of each microstate, E_j, are not equal, but we are still assuming that discrete energy levels exist, as dictated by quantum mechanics. Previously, we showed that the number of ways to distribute particles among the energy levels of the microstates is

$$\Omega = \frac{N!}{\prod_j N_j!} \cdot \prod_j g_j^{N_j}$$

There are some constraints on this equation. The total energy of the system must be equal to the energy of each quantized state, ϵ_i, times the number of particles in that energy level, N_i:

$$E = \sum_i N_i \cdot \epsilon_i \tag{17.10}$$

Furthermore, the sum of all the N_i values must equal the total number of particles in the system:

$$N = \sum_i N_i \tag{17.11}$$

(Note the slight difference in the definitions of the number of particles. N_i represents the number of particles in each energy level, and N_j (different subscript) represents the number of particles in each microstate. In a canonical ensemble, N_j is the same for each microstate, but there is no requirement that N_i is the same for all microstates.)

There is still the problem that the set of occupation numbers N_j can be anything, according to the principle of equal a priori probabilities. In fact, the total possible arrangements are truly astronomical, but we will ignore all but one: the *most probable arrangement*.

Consider a bar graph that plots the number of ways a combination can be made versus what we will call the compactness of the arrangement. By "compactness," we mean a general understanding of how many different microsystems participate in the specific arrangement. For instance, in Example 17.2 there were two particular arrangements in which two energy levels were populated and one arrangement in which three energy levels were populated. We can say that the three-level population was less compact than the other two, which were more compact in either a lower energy level or a higher energy level. Notice that the less compact arrangement had six possible combinations, but the two more compact arrangements had only three possible combinations each. If we plot the number of combinations versus the compactness—with each side of the plot representing either extreme in compactness and the middle representing the least compact arrangement—we get a graph like Figure 17.7.

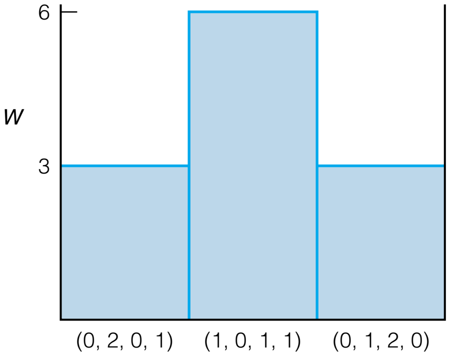


Figure 17.7 If we plot the number of possibilities versus the set of occupation numbers, we see the beginnings of a curve. See Figure 17.8 to see how this curve evolves.

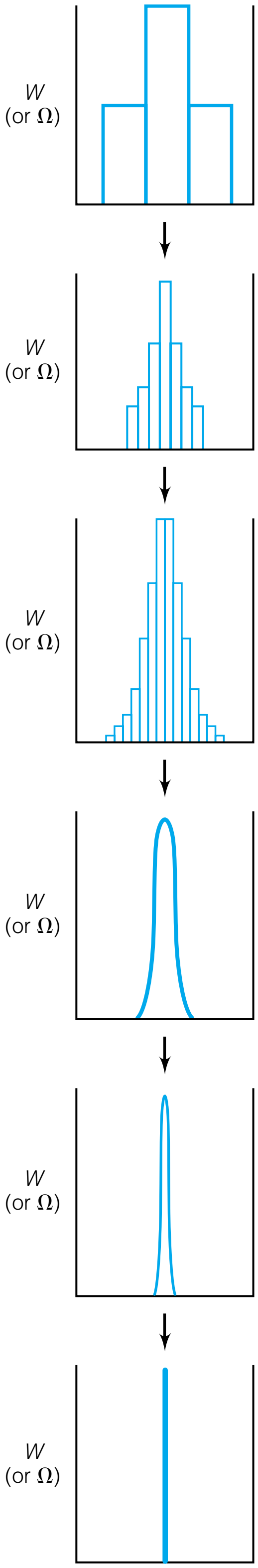


Figure 17.8 When the number of particles and possible arrangements gets larger and larger, the plot gets progressively narrower and narrower, even as the *x*-axis (representing the possible sets of occupation numbers) gets larger and larger.

If we increase the number of particles as well as the number of possible microstates, an interesting situation develops. As long as $\Omega \gg N$, the graphs start looking qualitatively like the curves in Figure 17.8. Of course, as N increases, Ω increases dramatically—the graphs in Figure 17.8 are not drawn to the same scales! But although the absolute heights of the peaks in Figure 17.8 increase factorially, the widths of the peaks do not increase at the same rate. Therefore, as N increases, the relative shape of the peaks gets narrower and narrower. This implies that although the number of possible combinations is growing, the number of combinations that are populated to any significant extent is getting progressively smaller. Thus, the combination corresponding to the most probable combination overwhelms any other combination.

What this argument implies is that we don't have to consider every possible set of occupation numbers in considering the microstates of an ensemble. For large N, only the most probable distribution needs to be considered.

If we have an expression for Ω in terms of the N_j values, we can take the derivative of that expression with respect to the set of N_j's and set it equal to zero [recall that at a maximum point in a plot, the derivative (that is, the slope) equals zero]. We can then derive some expression that might be meaningful. But we do have an expression for Ω in terms of N_j: equation 17.9. However, equation 17.9 can't be maximized by itself. It must be maximized in terms of the constraints on E (equation 17.10) and N (equation 17.11).

Rather than maximize Ω, we instead maximize $\ln \Omega$. We can do this because $\ln \Omega$ increases and decreases as Ω increases and decreases, so a maximum value of Ω corresponds to a maximum value of $\ln \Omega$. In addition, by maximizing $\ln \Omega$ we can take advantage of Stirling's approximation. From equation 17.9, we evaluate $\ln \Omega$ as

$$\ln \Omega = \ln \left(\frac{N!}{\prod_j N_j!} \cdot \prod_j g_j^{N_j} \right)$$

Using the properties of logarithms,* we simplify the right side of the equation to get

$$\ln \Omega = \ln N! + \sum_j (\ln g_j^{N_j} - \ln N_j!)$$

By invoking Stirling's approximation on both factorial terms and applying another property of logarithms,† we get

$$\ln \Omega = N \ln N - N + \sum_j (N_j \ln g_j - N_j \ln N_j + N_j)$$

We can distribute the summation sign through the three terms to get

$$\ln \Omega = N \ln N - N + \sum_j N_j \ln g_j - \sum_j N_j \ln N_j + \sum_j N_j$$

The summation $\Sigma\, N_j$ equals N, the total number of particles, so those two terms cancel on the right side. Again, we can use properties of logarithms and rearrange the remaining terms inside the summation to get

$$\ln \Omega = N \ln N + \sum_j N_j \ln \frac{g_j}{N_j} \qquad \textbf{(17.12)}$$

---

*Specifically, $\ln (a \cdot b/c) = \ln a + \ln b - \ln c$. Another way to express this is $\ln \Pi_j N_j = \Sigma_j \ln N_j$.

†Specifically, $\ln a^b = b \cdot \ln a$.

In order to maximize ln Ω in terms of the two constraints, we can combine the equations for ln Ω, N, and E into a single linear combination and maximize that resulting, three-term sum. However, we do not know the relative magnitudes of the individual terms in the sum. We will therefore multiply two of the three terms with a weighting factor. We use α as the weighting factor for N, and β as the weighting factor for E. This technique is referred to as *Langrange's method of undetermined multipliers* and gives us

$$\ln \Omega + \alpha \cdot N - \beta \cdot E$$

as the expression to minimize. (The negative sign on the last term is for our future convenience, and will be justified shortly.) Substituting for Ω, N, and E, we get

$$\left(N \ln N + \sum_j N_j \ln \frac{g_j}{N_j}\right) + \alpha \cdot \sum_i N_i - \beta \cdot \sum_i N_i \cdot \epsilon_i \tag{17.13}$$

as the expression to minimize.

Since the compactness of a distribution is dictated by the occupation numbers, we take the derivative of this expression with respect to the N_j values (all j of them) and require that they collectively be zero, as befits the maximum point in the plot of a function:

$$\frac{\partial}{\partial N_j}\left[\left(N \ln N + \sum_j N_j \ln \frac{g_j}{N_j}\right) + \alpha \cdot \sum_i N_i - \beta \cdot \sum_i N_i \cdot \epsilon_i\right] = 0 \tag{17.14}$$

for each value of N_j. Equation 17.14 thus gives us j expressions that must equal zero.

The derivative of $N \ln N$ with respect to N_j is zero, since $N \ln N$ is a constant. Even though N_j and N_i represent different occupation numbers, for a large enough system there will always be instances in which $N_i = N_j$. Therefore, the effect of the derivative in terms of j is to eliminate all the terms in the remaining summations except one, the one in which $N_i = N_j$. What remains are i equations of the form

$$\ln \frac{g_i}{N_i} - 1 + \alpha - \beta\epsilon_i = 0 \qquad i = 1, 2, 3, \ldots \tag{17.15}$$

For simplicity, we redefine the undetermined multiplier α as

$$\alpha \equiv \alpha - 1 \tag{17.16}$$

Rearranging, we get

$$\ln \frac{g_i}{N_i} = -\alpha + \beta\epsilon_i$$

$$\ln \frac{N_i}{g_i} = \alpha - \beta\epsilon_i$$

$$\frac{N_i}{g_i} = e^{\alpha - \beta\epsilon_i}$$

$$\frac{N_i}{g_i} = e^{\alpha} e^{-\beta\epsilon_i}$$

$$N_i = g_i e^{\alpha} e^{-\beta\epsilon_i} \tag{17.17}$$

If we sum the values of both sides of equation 17.17 over possible values of i, we get

$$\sum_i N_i = N = \sum_i g_i e^{\alpha} e^{-\beta\epsilon_i}$$

where we have used the fact that $\Sigma_i N_i = N$. Since e^α is a constant (e is a constant and α is a constant), we factor that term out to get

$$N = e^\alpha \sum_i g_i e^{-\beta\epsilon_i} \tag{17.18}$$

Notice what equation 17.18 gives us. The total number of particles N must satisfy an expression in terms of the degeneracies of the energy levels, g_i, and an exponential expression that is related to the energy of the ith quantum state. It is also dependent on some exponential e^α and the constant β, whose forms we don't know yet. But equation 17.18 suggests that there will be a relationship between the two constants α and β and the energy and number of particles in the system.

The expression $\Sigma_i g_i e^{-\beta\epsilon_i}$ is going to be a common one in statistical thermodynamics, so it is useful to give it a symbol. We define q as

$$q \equiv \sum_i g_i e^{-\beta\epsilon_i} \tag{17.19}$$

This quantity q is called the *partition function.* It plays a central role in statistical thermodynamics. Because we defined our system as a canonical ensemble, q is commonly called the canonical ensemble partition function.

Even though we don't know the absolute number of particles N_i in energy state ϵ_i, we can determine what *fraction* of the total particles are in that energy state (and then, if we know the total number of particles, we can calculate the absolute number N_i.) We do this by using the expressions in equations 17.17 and 17.18. The fraction is given by the expression N_i/N, which according to those equations is

$$\frac{N_i}{N} = \frac{g_i e^\alpha e^{-\beta\epsilon_i}}{e^\alpha \sum_i g_i e^{-\beta\epsilon_i}} = \frac{g_i e^\alpha e^{-\beta\epsilon_i}}{e^\alpha \cdot q}$$

The exponential e^α cancels:

$$\frac{N_i}{N} = \frac{1}{q} \cdot g_i e^{-\beta\epsilon_i} \tag{17.20}$$

Consider this expression. For any given distribution (and certainly for the most probable distribution) of a canonical ensemble, q is a constant that depends on the temperatures, numbers of particles, and volumes of the microstates. Degeneracy of the ith energy state is also a constant for a given substance, and e and β are also constants. Therefore, the only variable so far is ϵ_i, the energy of the quantum state. The population of any energy level is a negative exponential function of the value of the energy level above the ground state, a function that looks like Figure 17.9, that is, the population of the energy levels decreases exponentially with increasing energy. This type of population distribution is called the *Maxwell-Boltzmann distribution* (sometimes more concisely called the Boltzmann distribution). Notice that the α term is not present in equation 17.20. The implication here is that α is not much of a concern to us. However, the constant β remains, and determining the value of β is an important step in the development of statistical thermodynamics.

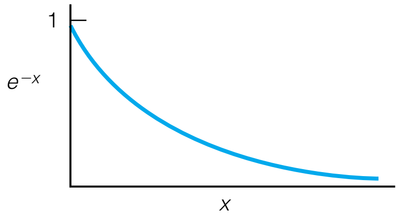


Figure 17.9 This is the general shape of a negative exponential, which is the heart of the Boltzmann distribution. Relating this to equation 17.20, it implies that the higher in energy a state is, the less it will be populated (as long as degeneracy is not considered).

The partition function q is still a part of equation 17.20, however. We can eliminate q by determining the ratio of the population of the ith energy level to the population of the k^{th} energy level:

$$\frac{\dfrac{N_i}{N}}{\dfrac{N_k}{N}} = \frac{\dfrac{1}{q} \cdot g_i e^{-\beta\epsilon_i}}{\dfrac{1}{q} \cdot g_k e^{-\beta\epsilon_k}}$$

The N and q terms cancel:

$$\frac{N_i}{N_k} = \frac{g_i e^{-\beta\epsilon_i}}{g_k e^{-\beta\epsilon_k}}$$

and we can combine the two exponentials algebraically:

$$\frac{N_i}{N_k} = \frac{g_i}{g_k} \cdot e^{-\beta(\epsilon_i - \epsilon_k)}$$

This expression is usually written as

$$\frac{N_i}{N_k} = \frac{g_i}{g_k} \cdot e^{-\beta \cdot \Delta\epsilon} \tag{17.21}$$

where $\Delta\epsilon$ is the difference in energies of the ith and kth states. Notice how the degeneracies do not automatically cancel.

A fractional population is numerically equivalent to a probability. The probability that any individual particle selected at random will be in the ith energy state is therefore

$$P_i = \frac{1}{q} \cdot g_i e^{-\beta\epsilon_i} \tag{17.22}$$

The reason we point this out is that now we can use some statistical perspectives to understand thermodynamic properties. For example, with the ideas from section 17.2, we can use

$$\bar{u} = \frac{\displaystyle\sum_{i=1}^{\substack{\text{possible}\\ \text{values}}} u_i \cdot P_i}{\displaystyle\sum_i P_i}$$

because we have an expression for P_i. Suppose we want to know what the average energy values of the microstates are. We can rewrite the above equation as

$$\bar{E} = \frac{\displaystyle\sum_i \epsilon_i \cdot \frac{1}{q} \cdot g_i e^{-\beta\epsilon_i}}{\displaystyle\sum_i \frac{1}{q} \cdot g_i e^{-\beta\epsilon_i}}$$

where $\bar{E}$ is the average energy and ϵ_i is the energy of each individual state. Because q is a constant for a given set of conditions, it can be factored out of every term in each sum and then canceled from both the numerator and denominator. Therefore,

$$\bar{E} = \frac{\displaystyle\sum_i \epsilon_i \cdot g_i e^{-\beta\epsilon_i}}{\displaystyle\sum_i g_i e^{-\beta\epsilon_i}} \tag{17.23}$$

Thus, we have a way to calculate the average energy $\bar{E}$ from a statistical consideration of the energies of the individual particles in the system. Further, we postulate that *the average energy $\bar{E}$ is equal to the thermodynamic energy E of the system.*

We need to determine what β is. In order to do this, we will have to use some equations from phenomenological thermodynamics. Recall that the first law of thermodynamics says that the change in energy of a system can be partitioned into heat and work. Using the variables from this chapter, we can write it as

$$dE = dq + dw$$

(Do not confuse q for heat with q for the partition function. Notice, also, that in this chapter we are using E for the total (that is, internal) energy and not U as in Chapters 2 and forward. This is common in statistical thermodynamics.) For an adiabatic change, dq equals 0, and the pressure-volume work performed by the system allows us to rewrite the above equation as

$$dE = -p \cdot dV$$

If we wanted to bring the dV term to the other side of the equation, we can derive an expression for the pressure of a system:

$$p = -\frac{\partial E}{\partial V}$$

For individual microstates in which the number of particles N_i remains the same, we can rewrite the above equation as

$$p_i = -\left(\frac{\partial \epsilon_i}{\partial V_i}\right)_{N_i} \tag{17.24}$$

Since the energy of the microstate, ϵ_i, depends on the microstate, so does the pressure p_i. If pressure is defined like this, then we can take the derivative of equation 17.23 with respect to V_i and get the average pressure, $\overline{p}$, just like we determined the average energy:

$$\overline{p} = \frac{-\sum_i \left(\frac{\partial \epsilon_i}{\partial V_i}\right)_{N_i} \cdot g_i e^{-\beta\epsilon_i}}{\sum_i g_i e^{-\beta\epsilon_i}} \tag{17.25}$$

However, increasing the number of microstates that have the same average pressure doesn't change the value for the overall pressure of the system. The average pressure of the microstates equals the average pressure of the entire system. That is,

$$\overline{p} = p_{\text{thermo}} \tag{17.26}$$

where p_{thermo} is the phenomenological, macroscopic, *measurable* pressure of our system. Equation 17.26 is the first direct connection between statistical thermodynamics and phenomenological thermodynamics.

In order to determine β, we start by taking the derivative of $\overline{E}$ (from equation 17.23) with respect to V, and the derivative of $\overline{p}$ (equation 17.25) with respect to β. In both cases, we have to apply the chain rule of derivation, and certain substitutions can be made. Ultimately (the steps won't be given here), we get

$$\left(\frac{\partial \overline{E}}{\partial V}\right) = -\overline{p} + \beta(\overline{Ep}) - \beta\overline{E} \cdot \overline{p} \tag{17.27}$$

$$\left(\frac{\partial \overline{p}}{\partial \beta}\right) = \overline{E} \cdot \overline{p} - (\overline{Ep}) \tag{17.28}$$

Substituting and rearranging:

$$\left(\frac{\partial \overline{E}}{\partial V}\right) + \beta\left(\frac{\partial \overline{p}}{\partial \beta}\right) = -\overline{p} \tag{17.29}$$

Compare this equation with another equation that can be derived from thermodynamics:

$$\left(\frac{\partial E}{\partial V}\right) + \frac{1}{T}\left[\frac{\partial p}{\partial(1/T)}\right] = -p \qquad \textbf{(17.30)}$$

where we have used E to represent the internal energy. These two equations are strikingly similar. They imply that β is related to $1/T$. β is not *equal* to $1/T$, because a proportionality factor would cancel from equation 17.30. β is certainly proportional to $1/T$:

$$\beta \propto \frac{1}{T}$$

As usual in equations like this, a proportionality can be written as an equality by introducing the appropriate proportionality constant. But rather than putting this constant in the numerator, the convention is to put it in the denominator. Giving the proportionality constant the symbol k, we have

$$\beta = \frac{1}{kT} \qquad \textbf{(17.31)}$$

The constant k is called *Boltzmann's constant* and has a value of 1.381×10^{-23} J/K. The expression for the partition coefficient q becomes

$$q = \sum_i g_i e^{-\epsilon_i/kT} \qquad \textbf{(17.32)}$$

All previous equations with β can be modified accordingly.

Example 17.3

Consider the diagram in Figure 17.5 with the four energy levels. Assuming that the energy levels are fourfold degenerate (that is, $g_i = 4$) and that the energy levels have values of 0.00, 1.00, 2.00, and 3.00×10^{-21} J, what is the value of the partition function at 25°C = 298 K? What is the value for q if the energy levels are 0.00, 1.00, 2.00, and 3.00×10^{-19} J?

Solution

The summation from equation 17.32 can be set up as

$$\begin{aligned} q = {} & 4 \cdot \exp\left[-\frac{0.00 \times 10^{-21}\text{ J}}{(1.381 \times 10^{-23}\text{ J/K})(298\text{ K})}\right] \\ & + 4 \cdot \exp\left[\frac{1.00 \times 10^{-21}\text{ J}}{(1.381 \times 10^{-23}\text{ J/K})(298\text{ K})}\right] \\ & + 4 \cdot \exp\left[-\frac{2.00 \times 10^{-21}\text{ J}}{(1.381 \times 10^{-23}\text{ J/K})(298\text{ K})}\right] \\ & + 4 \cdot \exp\left[\frac{3.00 \times 10^{-21}\text{ J}}{(1.381 \times 10^{-23}\text{J/K})(298\text{ K})}\right] \end{aligned}$$

$$q = 4 \cdot 1 + 4 \cdot 0.784 + 4 \cdot 0.615 + 4 \cdot 0.482$$

$$q = 11.524$$

where exp is the same exponential function as e but allows long exponents to appear in a more readable form. All of the units cancel, and q is just a number. For the larger values for the energy levels, it can be shown that

$$q = 4 \cdot 1 + 4 \cdot 2.80 \times 10^{-11} + 4 \cdot 7.84 \times 10^{-22} + 4 \cdot 2.19 \times 10^{-32}$$

$$q \approx 4$$

This second example shows how sensitive q is to the values of the energy levels.

For the second set of energy levels in the above example, the fact that q is approximately equal to the number of levels suggests a molecular interpretation of the partition function: q is a measure of the number of energy states that are available to a particle at any particular temperature. Thus, for low-energy states at a given temperature, many of those states can be populated by thermal energy. In the above example, approximately 12 of the lower-energy states (recall that each level is fourfold degenerate) could be populated at 298 K. But if the higher-energy states are considered, only the ground state (degeneracy = 4) is generally populated, so a partition function value of 4 is consistent with this interpretation of q.

17.5 Thermodynamic Properties from Statistical Thermodynamics

Now that we have established the complete form of our partition function, how can we determine thermodynamic properties from it? We will start with energy. The total energy of the ensemble is given by equation 17.10:

$$E = \sum_i N_i \cdot \epsilon_i$$

Substituting for N_i from equations 17.20 and 17.31:

$$E = \sum_i \frac{N}{q} \cdot g_i e^{-\epsilon_i/kT} \cdot \epsilon_i$$

$$E = N \cdot \frac{1}{q} \cdot \sum_i g_i e^{-\epsilon_i/kT} \cdot \epsilon_i \tag{17.33}$$

Consider briefly the derivative of equation 17.32 with respect to temperature:

$$\frac{\partial q}{\partial T} = \frac{\partial}{\partial T} \sum_i g_i e^{-\epsilon_i/kT}$$

$$= \sum_i g_i \cdot \frac{\partial}{\partial T} e^{-\epsilon_i/kT}$$

$$= \sum_i g_i \cdot e^{-\epsilon_i/kT} \cdot \frac{\epsilon_i}{kT^2}$$

$$\frac{\partial q}{\partial T} = \frac{1}{kT^2} \sum_i g_i e^{-\epsilon_i/kT} \cdot \epsilon_i$$

If we divide both sides by q, we get

$$\frac{1}{q} \cdot \frac{\partial q}{\partial T} = \frac{1}{q} \cdot \frac{1}{kT^2} \sum_i g_i e^{-\epsilon_i/kT} \cdot \epsilon_i$$

According to the rules of calculus, the left side of the above equation is $(\partial \ln q/\partial T)$. Moving the kT^2 term to the left side, we have

$$kT^2 \frac{\partial \ln q}{\partial T} = \frac{1}{q} \cdot \sum_i g_i e^{-\epsilon_i/kT} \cdot \epsilon_i$$

The right side of this equation is most of the right side of equation 17.33. Substituting:

$$E = NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_V \tag{17.34}$$

where we are indicating the constant-volume condition explicitly. Equation 17.34 is an amazing result: if we know how the logarithm of q varies with temperature, we can calculate the energy of our system. This expression demonstrates the central role that the partition function plays in statistical thermodynamics.

We have already introduced the pressure as a thermodynamic variable. In a fashion similar to how we got equation 17.34, it can be shown that

$$p = NkT\left(\frac{\partial \ln q}{\partial V}\right)_T \tag{17.35}$$

From the first-law relationship between the internal energy and H, the enthalpy:

$$H = E + pV$$

$$H = E + NkT$$

$$H = NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_V + NkT$$

from which we can get

$$H = NkT\left(T\frac{\partial \ln q}{\partial T} + 1\right) \tag{17.36}$$

Statistical thermodynamics therefore gives expressions for all of the basic thermodynamic state functions, and they all depend on the partition function q.

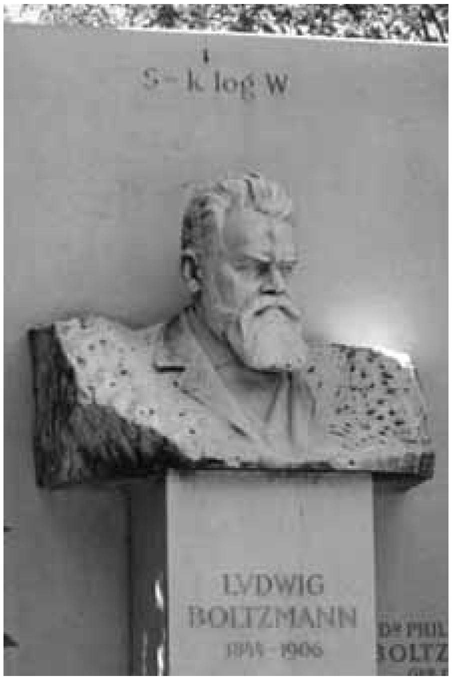
In order to get expressions for Gibbs free energy G and the Helmholtz energy A, we will need an expression for the entropy, S. The statistical thermodynamic approach for S is somewhat different. Rather than derive a statistical thermodynamic expression for S (which can be done but will not be given here*), we present Ludwig Boltzmann's 1877 seminal contribution relating entropy S and the distribution of particles in an ensemble Ω:

$$S \propto \ln \Omega \tag{17.37}$$

The proportionality constant is also Boltzmann's constant, k (the same k used to define β). This definition of entropy becomes

$$S = k \ln \Omega \tag{17.38}$$

This postulate is so important in the development of statistical thermodynamics that it is carved on Boltzmann's tombstone (Figure 17.10).



Courtesy of Frantisek Zboray, Vienna.

Figure 17.10 Boltzmann's assumption that entropy is proportional to the number of possible arrangements is so important to statistical thermodynamics that it is engraved on Boltzmann's tombstone in Vienna.

Using equation 17.38 as a starting point, we can substitute for Ω from equation 17.9 and get

$$S = k \ln\left(\frac{N!}{\prod_j N_j!} \cdot \prod_j g_j^{N_j}\right)$$

$$= k \ln\left(N! \cdot \prod_j \frac{g_j^{N_j}}{N_j!}\right) \tag{17.39}$$

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*Interested readers can find details in D. McQuarrie, *Statistical Thermodynamics*, University Science Books, Mill Valley, Calif., 1973.

where the second equation is simply an algebraic rearrangement of the first one. Rearranging by applying the properties of logarithms (see the footnotes earlier in this chapter):

$$S = k\left(\ln N! + \sum_j \ln g_j^{N_j} - \sum_j \ln N_j!\right)$$

We can now apply Stirling's approximation to the ln $N!$ and ln $N_i!$ terms:

$$S = k\left(N \ln N - N + \sum_j \ln g_j^{N_j} - \sum_j (N_j \ln N_j - N_j)\right)$$

Distributing the last summation through both terms:

$$S = k\left(N \ln N - N + \sum_j \ln g_j^{N_j} - \sum_j N_j \ln N_j + \sum_j N_j\right)$$

We recognize that $\Sigma\, N_j$ is equal to N, the total number of particles. Therefore, this summation cancels with the $-N$ term earlier in the brackets. So

$$S = k\left(N \ln N + \sum_j \ln g_j^{N_j} - \sum_j N_j \ln N_j\right) \tag{17.40}$$

We can further simplify the above equation by combining the two remaining summations algebraically, once again taking advantage of the properties of logarithms. We get

$$S = k\left(N \ln N + \sum_j N_j \ln \frac{g_j}{N_j}\right) \tag{17.41}$$

The term $\ln(g_j/N_j)$ can be expressed in terms of the Boltzmann distribution, equation 17.20, if we take the logarithm of that equation. This introduces a term in the energies ϵ_i. Using the fact that $\Sigma_i \epsilon_i = E$, the total energy of the system, and recognizing that we have an expression for E in terms of q, we can show that equation 17.41 is equivalent to

$$S = Nk\left[T\left(\frac{\partial \ln q}{\partial T}\right)_V + \ln q\right] \tag{17.42}$$

However, in the case of entropy the identity of the particles is a factor. In section 17.2 we assumed that we could tell the difference between individual particles; that is, we assumed they were distinguishable. In fact, at the atomic level we cannot distinguish between individual, identical particles; atoms and molecules are macroscopically *indistinguishable.* This means that we are overcounting the total number of possible distributions for Ω. The factor that fixes this overcounting is a factor of $N!$ in the denominator of Ω. (That is, there are $1/N!$ times fewer distributions for indistinguishable particles than for distinguishable particles.) When this factor is considered, the equations become

$$\Omega_{\text{indist}} = \frac{1}{N!} \cdot \frac{N!}{\prod_j N_j!} \cdot \prod_j g_j^{N_j}$$

and the final expression for entropy becomes

$$S = Nk\left[T\left(\frac{\partial \ln q}{\partial T}\right)_V + \ln \frac{q}{N} + 1\right] \tag{17.43}$$

This is the more accurate expression for the entropy, S.

It is the statistical thermodynamical approach to entropy that relates this state function to the well-known and classic relationship with disorder. *Disorder* can be thought of as a measure of the number of possible places objects *can* occupy. This is one way of defining Ω. And when such a number of places are possible, statistics shows that they will be occupied: a high disorder content is directly related to a high absolute entropy. The qualitative relationship is very useful for predictive purposes. But be aware that the relationship also has direct quantitative consequences. We will be able to determine those quantities shortly—when we find q, the partition function.

The second and third law of thermodynamics can be understood in terms of the disorder concept of entropy. For an isolated system in which there is no transfer of mass or energy, a spontaneous change can be thought of as a change in which the particles of the system access more possible arrangements. That is, for a spontaneous process from state 1 to state 2,

$$\Omega\text{ (state 2)} > \Omega\text{ (state 1)}$$

From equation 17.40, which is Boltzmann's postulate for the definition of S, we get for the ΔS of a spontaneous process:

$$\Delta S = k\ln[\Omega\text{ (state 2)}] - k\ln[\Omega\text{ (state 1)}]$$

$$\Delta S = k\ln\frac{\Omega\text{ (state 2)}}{\Omega\text{ (state 1)}}$$

which is always a positive number: the fraction $[\Omega\text{ (state 2)}]/[\Omega\text{ (state 1)}]$ is always >1, and the logarithm of a number greater than 1 is positive. Thus, a spontaneous change occurs with an increase in the total entropy—or "disorder"—of the system. See Figure 17.11.

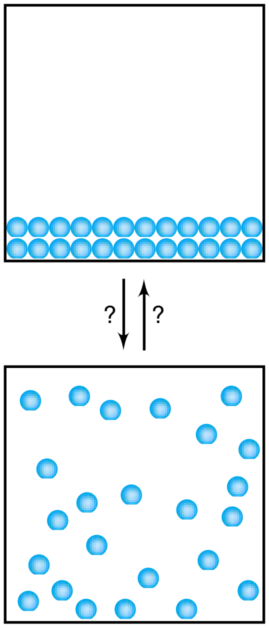

Figure 17.11 Which direction is the spontaneous one from a strict disorder perspective? It is also the spontaneous direction from a strict entropy perspective.

For the third law, we can substitute the expression for q into equation 17.42 and take the derivative of q with respect to temperature. We get

$$S = k\ln(\Sigma\, g_i\cdot e^{-\epsilon_i/kT}) + \frac{1}{T}\,\frac{\Sigma\,\epsilon_i\cdot g_i\cdot e^{-\epsilon_i/kT}}{\Sigma\, g_i\cdot e^{-\epsilon_i/kT}}$$

If we take the limit of this expression as $T \rightarrow 0$,* we would find that

$$\lim_{T\to 0} S = k\ln g_0$$

where g_0 is the degeneracy of the ground state. In the limit of $T \rightarrow 0$, the lowest possible energy states are the only states that are populated.

If the ground state is nondegenerate, then $g_0 = 1$ and S is exactly zero, in exact agreement with the third law of thermodynamics. This would be strictly true if there was only a single particle in the system. In most systems, there are usually enough atoms and molecules that we can speak of their quantities in molar amounts, that is, on the order of 10^{20} and greater. Therefore, g_0 can be at least 10^{20} in real systems. Does this lead to a violation of the third law?

Not really. The logarithm of 10^{20} is about 46, and multiplying $\ln(10^{20})$ by Boltzmann's constant, 1.381×10^{-23} J/K, gives about 6×10^{-22} J/K—an immeasurably small amount of entropy (especially considering that molar entropies, which *are* measured, are on the order of dozens or hundreds of J/K, 25 or more orders of magnitude higher). We would need something on the order of $10^{10^{19}}$ atoms before the entropy at absolute zero would be noticeable, and to give you an idea of how big that number is, there isn't room in the visible universe for that many atoms! Therefore, for all practical purposes, we can indeed say that S approaches zero as the temperature approaches absolute zero,

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*The limit can be determined by applying L'Hôpital's rule from calculus.

as long as the other relevant conditions apply to the system. Statistical thermodynamics' definition of entropy is thus consistent with the third law of thermodynamics as developed by phenomenological thermodynamics.

Knowing the relationship between q and S, it is simple mathematics to determine what the Helmholtz energy, A, and the Gibbs energy, G, are in terms of the partition function. They are

$$A = -NkT \ln \frac{q}{N} \tag{17.44}$$

$$G = -NkT \left(\ln \frac{q}{N} - 1 \right) \tag{17.45}$$

Notice that both A and G are *directly* related to q, rather than related to a derivative of q. Although this is an artifact of the mathematics and the definition of the ensemble, there should be some wonder that the important state functions (G and A) are so intimately related to the partition function q, which becomes the central focus in statistical thermodynamics.

Finally, since the chemical potential μ_i for the ith chemical species is the basic focus in chemical equilibrium, we can easily define μ_i in terms of q:

$$\mu_i = \left(\frac{\partial G}{\partial N_i} \right)$$

Therefore, from equation 17.45:

$$\mu_i = -kT \ln \frac{q}{N_i} \tag{17.46}$$

Chemical potential is also directly related to q.

17.6 The Partition Function: Monatomic Gases

The previous section made it clear that all thermodynamic state functions are in some way related to the partition function q. This means that in order to know these state functions, we need to know what q is. How?

First, recall that q is simply a sum of negative exponentials of the discrete energy levels:

$$q = \sum_i g_i \cdot e^{-\epsilon_i/kT}$$

Technically this is an infinite sum, because there are an infinite number of possible energy levels for any particle (which is a general conclusion of both classical and quantum mechanics). However, because q is defined in terms of *negative* exponentials, each successive term gets smaller, so the potentially infinite number of terms in the summation does not automatically imply that $q = \infty$.

Second, if the energy levels are close enough together, then each term in the summation is infinitesimally close to the previous term, and also infinitesimally close to the next term. It can be well approximated that rather than a sum of discrete terms, q can be written as an integral of a continuous function:

$$q = \sum_i g_i \cdot e^{-\epsilon_i/kT} \longrightarrow \int_{i=0}^{\infty} g_i \cdot e^{-\epsilon_i/kT}\, di \tag{17.47}$$

In order to determine a theoretical value of a partition function, we need an expression for the energy levels ϵ_i.

For atomic and molecular systems, we actually have such expressions: they come from the application of quantum mechanics to the translations, rotations, vibrations, and electronic states of atoms and molecules. Admittedly, Boltzmann didn't have quantum mechanics, since he developed the rudiments of statistical mechanics about 50 years before quantum mechanics was formulated. In fact, some of his expressions are incorrect by not including Planck's constant (Boltzmann was unaware of its existence for most of his life). But in the calculation of thermodynamic values, the Planck's constants cancel. Their omission was, ultimately, unnoticed. However, in the material to come, we will use the quantum-mechanical basis of energy levels.

We start by assuming that our sample consists of a monatomic gas, like He or Ne (or any other monatomic gas, like Hg vapor). Such a sample has only three types of energy states: electronic, nuclear, and translational. Of these three, electronic and nuclear states are states *within* the atoms. Only translational energy states relate the position of the atom as a whole, rather than relating the relative positions of the subatomic particles of the atom.

The partition function of a monatomic gas is a product of three separate partition functions defined by the translational energy levels, the electronic energy levels, and the nuclear energy levels:

$$q = q_{\text{trans}} \cdot q_{\text{elect}} \cdot q_{\text{nucl}} \tag{17.48}$$

Further, we will presume at this point that the translational partition function, q_{trans}, is the major contributor to the thermodynamic properties of a monatomic gas. (We will justify this by using the kinetic theory of gases, which is covered in Chapter 19. The relative contributions of q_{elect} and q_{nuc} will be considered in Chapter 18.) Therefore, for a monatomic ideal gas, we are assuming that

$$q = q_{\text{trans}}$$

How shall we model the translational motions of monatomic gases? Well, we can apply the particle-in-a-box approximation to the straight-line motions of the atoms in three-dimensional space. From Chapter 10, we know that for a particle in a three-dimensional box, the quantum-mechanically allowed energy levels are

$$\epsilon = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

The variable m is the mass of the particle in the box, and so in this case represents the mass of the *individual gaseous atom or molecule,* not the molar mass. For simplicity's sake, we will arbitrarily assume that we are working in a cubic system, so that $a = b = c$:

$$\epsilon = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \tag{17.49}$$

In terms of the volume of the system V, if the system is cubic, then $V = a^3$. Therefore, a^2 must equal $V^{2/3}$. Equation 17.49 becomes

$$\epsilon = \frac{h^2}{8mV^{2/3}}(n_x^2 + n_y^2 + n_z^2) \tag{17.50}$$

Therefore, our expression for q is (assuming that the translational states are all singly degenerate)

$$q = \sum \exp\left(\frac{-\frac{h^2}{8mV^{2/3}}(n_x^2 + n_y^2 + n_z^2)}{kT}\right)$$

$$= \sum \exp\left(-\frac{h^2(n_x^2 + n_y^2 + n_z^2)}{8mV^{2/3}kT}\right)$$

$$q = \sum_{n_z} \exp\left(\frac{-h^2 n_x^2}{8mV^{2/3}kT}\right) \cdot \sum_{n_y} \exp\left(\frac{-h^2 n_y^2}{8mV^{2/3}kT}\right) \cdot \sum_{n_z} \exp\left(\frac{-h^2 n_z^2}{8mV^{2/3}kT}\right) \qquad \textbf{(17.51)}$$

where the individual summations are now over the *x*, *y*, and *z* translational quantum numbers. All levels of one-dimensional particles-in-boxes are singly degenerate.

Since there is usually no preferential dimension for a three-dimensional system (a condition described as "isotropic"), then n_x is calculationally equivalent to n_y, which is calculationally equivalent to n_z. Also, because the system is assumed to be cubic, the quantized energies will be the same in all three dimensions. This means that the three terms in equation 17.51 can be combined into the third power of a single term:

$$q = \left[\sum_n \exp\left(\frac{-h^2 n^2}{8mV^{2/3}kT}\right)\right]^3 \qquad \textbf{(17.54)}$$

We have removed the subscript from the general translational quantum number *n*.

We now take the mathematical leap inferred by equation 17.47: if the individual terms in 17.52 are close enough together, we can approximate the (infinite) sum as an integral:

$$q = \left[\int_{n=0}^{\infty} \exp\left(\frac{-h^2 n^2}{8mV^{2/3}kT}\right) dn\right]^3 \qquad \textbf{(17.53)}$$

The variable in the integral is *n*, the translational quantum number. This integral has the form and solution

$$\int_{x=0}^{\infty} e^{-ax^2}\, dx = \frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$$

(see Appendix 1), where in the case of equation 17.53 the expression for the constant *a* is

$$\frac{h^2}{8mV^{2/3}kT}$$

We can therefore substitute a definite expression for the integral. We have

$$q = \left[\frac{1}{2}\left(\frac{\pi}{\frac{h^2}{8mV^{2/3}kT}}\right)^{1/2}\right]^3$$

Rearranging all of the terms and distributing through the powers, we get

$$q_{\text{trans}} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \cdot V \qquad \textbf{(17.54)}$$

where the volume variable *V* has been algebraically removed from the parentheses. The "trans" subscript has been added to remind ourselves that we are determining the partition function with respect to the translation of the atoms. Again, in equation 17.54 the variable *m* represents the mass of the *individual* gas particle.

Equation 17.54 is a useful conclusion. The (translational) partition function, originally defined as an infinite sum of negative exponentials of the energy levels, is equal to an expression in terms of the mass of the gas particles, the absolute temperature, the system volume, and some fundamental universal constants. This expression lets us calculate explicit values for q, which can then be used to determine values for energy, entropy, heat capacity, and so on. These calculated values—determined from a statistical rather than a phenomenological perspective—can then be compared to experimental values. We will thus get the first chance to see how well a statistical approach to thermodynamics compares with experiment.

Remember that q is unitless, since it is simply the sum of exponential functions, so all of the units in equation 17.54 will ultimately cancel. However, we will have to convert some units, particularly units of volume. Typically, volumes are expressed in units of liters. In order for the units to cancel properly, it is easiest if volume is expressed in units of cubic meters, m^3. Recall that the liter can be defined as a cube having sides 1.00 decimeter (1.00 dm) in length. Since a decimeter is 0.1 meter, we will take advantage of the conversion factor

$$1 \text{ L} = 0.001 \text{ m}^3 \tag{17.55}$$

Units will also work out if we express (molar) mass quantities in units of kg, not g.

Example 17.4

Calculate q_{trans} for 1 mole of He at standard thermodynamic conditions ($T = 298$ K, $V = 24.5$ L). The molar mass of He is 4.0026 g.

Solution

Keeping equation 17.55 in mind, the volume of 1 mole of He in cubic meter units is 0.0245 m^3. Also, we should express the mass of one atom of He in kg units: $(0.0040026 \text{ kg})/(6.02 \times 10^{23}) = 6.65 \times 10^{-27}$ kg. For q_{trans}, we get

$$q = \left[\frac{2 \cdot 3.14159(6.65 \times 10^{-27} \text{ kg})(1.381 \times 10^{-23} \text{J/K})298 \text{ K}}{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})^2}\right]^{3/2} 0.0245 \text{ m}^3$$

First we will work out the numbers. When we combine all of the numerical values (not forgetting, of course, the 3/2 power on the brackets), we get

$$\text{number} = 1.90 \times 10^{29}$$

Now we will examine the units. They are

$$\left(\frac{\text{kg} \cdot \dfrac{\text{J}}{\text{K}} \cdot \text{K}}{(\text{J}\cdot\text{s})^2}\right)^{3/2} \cdot \text{m}^3$$

Consider the units inside the parentheses first. The units of K cancel in the numerator, and one of the J units cancels in the numerator and the denominator. We have remaining

$$\frac{\text{kg}}{\text{J}\cdot\text{s}^2}$$

Remember, however, that the unit joule is a compound unit and equal to $(\text{kg}\cdot\text{m}^2)/\text{s}^2$. Substituting:

$$\frac{\text{kg}}{\dfrac{\text{kg} \cdot \text{m}^2}{\text{s}^2} \cdot \text{s}^2} = \frac{\text{kg}}{\text{kg} \cdot \text{m}^2} = \frac{1}{\text{m}^2}$$

Raising this unit to the power of 3/2 and including the m^3 unit from the volume term, we have

$$\left(\frac{1}{\text{m}^2}\right)^{3/2} \cdot \text{m}^3 = \frac{1}{\text{m}^3} \cdot \text{m}^3 = 1$$

That is, all of the units cancel, as they should! Combining the numerical part of the answer with the units part of the answer, we get

$$q = 1.90 \times 10^{29}$$

with no units. This is a very large number!

17.7 State Functions in Terms of Partition Functions

The importance of the partition function in statistical thermodynamics is that if we know q, we can determine thermodynamic properties. Indeed, almost all of the thermodynamic state functions can be written in terms of the change of the partition function as some state variable, T or V, changes. (Only A and G depend directly on q, and on the natural logarithm of q at that. This fact does not obviate the discussion to follow.)

Now that we have an expression for q, we can take those derivatives, since T and V are part of the expression for q. We can therefore derive expressions for various state functions.

We start with E, the total energy of our ensemble. According to equation 17.34,

$$E = NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_V = NkT^2\left(\frac{1}{q}\frac{\partial q}{\partial T}\right)_V$$

The derivative of q with respect to T (at constant V) is easy to determine:

$$\begin{aligned}\frac{\partial q}{\partial T} &= \frac{\partial}{\partial T}\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \cdot V\right] \\ &= \left(\frac{2\pi mk}{h^2}\right)^{3/2} V \cdot \frac{\partial}{\partial T}T^{3/2} \\ &= \left(\frac{2\pi mk}{h^2}\right)^{3/2} V \cdot \frac{3}{2} \cdot T^{1/2}\end{aligned}$$

If we take this expression and divide by q itself, almost all of the terms will cancel:

$$\frac{\left(\dfrac{2\pi mk}{h^2}\right)^{3/2} V \cdot \dfrac{3}{2} \cdot T^{1/2}}{\left(\dfrac{2\pi mkT}{h^2}\right)^{3/2} \cdot V}$$

The only thing remaining is $3/2 \cdot 1/T$. Therefore, for the energy of the particles in the system:

$$E = NkT^2 \cdot \frac{3}{2} \cdot \frac{1}{T}$$

$$E = \frac{3}{2}NkT \tag{17.56}$$

This is similar to the expression we get using the kinetic theory of gases (which we will consider in a later chapter). Statistical thermodynamics therefore yields the same answer as other physical chemical theories.

We can also determine an expression involving pressure, since we know that

$$p = NkT\left(\frac{\partial \ln q}{\partial V}\right)_T = NkT\left(\frac{1}{q}\frac{\partial q}{\partial V}\right)_T$$

The derivative of q with respect to volume, $\partial q/\partial V$, is simply $(2\pi mkT/h^2)^{3/2}$. Substituting:

$$p = NkT\frac{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}}{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\cdot V}$$

$$p = \frac{NkT}{V} \tag{17.57}$$

This rearranges to

$$pV = NkT \tag{17.58}$$

Compare this to the ideal gas law: it is identical provided that

$$R \equiv Nk \tag{17.59}$$

where R represents the ideal gas law constant. Boltzmann's constant therefore provides a statistical thermodynamic foundation for the ideal gas law constant. In fact, if $N = N_A$ (Avogadro's number),

$$R = N_Ak \tag{17.60}$$

and we have the molar ideal gas law $p\overline{V} = RT$. Of course, for n moles of gas, this becomes the most general form of the ideal gas law, $pV = nRT$. The relationship between R and k is also illustrated by the units used to describe the two constants.

Example 17.5

Verify equation 17.60, using SI units of energy for R and k, and then determine the value of k in units of L·atm/K.

Solution

We can use the values of any two of the variables in equation 17.60 and calculate the third and compare our result to a tabulated value. For this example, let us pick values for k and N_A: $k = 1.381 \times 10^{-23}$J/K and $N_A = 6.022 \times 10^{23}$/mol. We find that

$$R = (6.022 \times 10^{23}/\text{mol}) \cdot 1.381 \times 10^{-23}\,\frac{\text{J}}{\text{K}}$$

$$R = 8.316\,\frac{\text{J}}{\text{mol·K}}$$

which is off by only 0.02% from the accepted value.

In order to determine k in units of L·atm/K, we will need to use the value for R that has L·atm units. Using $R = 0.08205$ L·atm/(mol·K), we substitute for different constants this time:

$$0.08205\frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} = 6.022 \times 10^{23}/\text{mol}\cdot k$$

$$k = \frac{0.08205\dfrac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}}{6.022 \times 10^{23}/\text{mol}}$$

The mole units cancel on both sides of the fraction; for k we get:

$$k = 1.363 \times 10^{-25}\frac{\text{L}\cdot\text{atm}}{\text{K}}$$

which is a perfectly good value for k if the units are appropriate otherwise.

We have seen that statistical thermodynamics gives the same translational (that is, internal) energies and pressures that we find from other, phenomenological perspectives. But values for A and G depend on the entropy of our gaseous sample. It remains to be seen how (or rather, if!) statistical thermodynamics' predictions for S agree with phenomenological values of entropy.

Using equation 17.43:

$$S = Nk\left[T\left(\frac{\partial \ln q}{\partial T}\right)_V + \ln\frac{q}{N} + 1\right]$$

we can make some similar substitutions to get an expression for S. Without going through the math (which is left to the end-of-chapter exercises), we get

$$S = Nk\left\{\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\cdot\frac{kT}{p}\right] + \frac{5}{2}\right\} \qquad \textbf{(17.61)}$$

Equation 17.61 is one form of what is called the *Sackur-Tetrode equation*. It provides what is probably the best example of how well statistical thermodynamics applies to gaseous systems, because we can measure absolute entropies. The following example illustrates.

Example 17.6

What is the absolute entropy of 1 mole of He at 25.0°C and 1.000 atm pressure? Compare this with the tabulated value of 126.04 J/(mol·K). Don't forget that proper units are necessary.

Solution

The "proper units" warning was to remind us that masses should be expressed in units of kg, and that volumes should be expressed in m^3. For He, the mass $m = 6.65 \times 10^{-27}$ kg (see Example 17.4), and $1\ \text{m}^3 = 1000$ L. From equation 17.61, we have

$$S = (6.022 \times 10^{23}/\text{mol})\left(1.381 \times 10^{-23}\,\frac{\text{J}}{\text{K}}\right)$$
$$\times\left(\ln\left\{\left[\frac{2\pi(6.65 \times 10^{-27}\ \text{kg})(1.381 \times 10^{-23}\frac{\text{J}}{\text{K}})(298\ \text{K})}{(6.626 \times 10^{-34}\text{J}\cdot\text{s})^2}\right]^{3/2}\right.\right.$$
$$\left.\left.\times\frac{\left(1.381 \times 10^{-23}\frac{\text{J}}{\text{K}}\right)(298\ \text{K})}{(1.000\ \text{atm})\left(\dfrac{101.32\ \text{J}}{\text{L}\cdot\text{atm}}\right)}\cdot\frac{1\ \text{m}^3}{1000\ \text{L}}\right\} + \frac{5}{2}\right)$$

Note the presence of the liter-to-m^3 conversion and the joule-to-L·atm conversion in the appropriate places. Evaluating this lengthy but straightforward expression, we get

$$S = 126.07 \frac{\text{J}}{\text{mol·K}}$$

This calculated value of S is virtually the same as the experimental value. (The variance is 0.02%.)

The experimental value of S and its calculated value using statistical thermodynamics in the above example are virtually identical! At this point in our development of statistical thermodynamics, absolute entropy is our best evidence that the ideas behind statistical thermodynamics are valid and useful in understanding the thermodynamic behavior of systems (at least systems of gases). Table 17.1 compares experimental values with calculated values of S for several monatomic gases. You can see that the agreement is very, very good.

Table 17.1 Comparison of calculated and experimental entropy, S, for monatomic gases[a]

Gas	S_{calc}	S_{expt}
He	126.07	126.04
Ne	146.22	146.22
Ar	154.74	154.73
Kr	163.98	163.97
Xe	169.58	169.57

[a] All values are in units of J/(mol·K) at conditions of 298 K, 1.00 atm.

Now that an expression for S has been determined (and verified), we can derive expressions for G and A in terms of the partition function q. Without going through the derivations, we have

$$A = -NkT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \cdot \frac{V}{N} \right] \tag{17.62}$$

$$G = -NkT \left\{ \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \cdot \frac{V}{N} \right] - 1 \right\} \tag{17.63}$$

Notice that of the two, the expression for A is simpler. This is a consequence of the fact that we have defined our system in terms of microstates that have the same volume, V, and temperature, T. These two variables are the natural variables for A, the Helmholtz energy. It is not surprising, then, that the expression for A in statistical thermodynamics is relatively simple. If we instead defined our ensemble in terms of microstates that have the same pressure and temperature, we would find that the expression for G, the Gibbs free energy, is relatively straightforward because p and T are the natural variables for G.

Finally, we define a new parameter. It is not a state function, but a parameter that has parallels in quantum mechanics. Notice that the part of q in the term

$$\left(\frac{2\pi mkT}{h^2} \right)^{3/2}$$

has SI units of 1/m^3. Therefore, the term

$$\left(\frac{2\pi mkT}{h^2} \right)^{1/2}$$

(which is the cube root of the previous expression) has units of 1/m. The *reciprocal* of this expression therefore has units of length, meters. We define the reciprocal of this expression as Λ (the Greek capital letter lambda), the *thermal de Broglie wavelength:*

$$\Lambda = \left(\frac{h^2}{2\pi mkT} \right)^{1/2} \tag{17.64}$$

The original de Broglie wavelength was defined in terms of the momentum, p, of a particle:

$$\lambda = \frac{h}{p} = \frac{h}{mv} \tag{17.65}$$

where in the second equality we have made a substitution using $p = mv$. Comparing equations 17.64 and 17.65, we find that the classical momentum p is equivalent to $(2\pi mkT)^{1/2}$. Actually, this equivalency is only suggestive, not exact, since the expression for Λ is ultimately derived from the most probable distribution and is related more to the average momentum, $\overline{p}$, of the gas particles. A similar relationship can be determined from the expressions for the energies of the gas particles. For N particles, equation 17.56 says that

$$E = \tfrac{3}{2}NkT$$

Classically, the energy of motion for N particles is

$$E = N \cdot \frac{p^2}{2m}$$

Equating the two expressions and solving for p, we find that p is equivalent to $(3mkT)^{1/2}$, which is almost the same expression. Again, this is only suggestive, not exact, but such relationships are expected if two widely different perspectives on thermodynamics predict similar values for measurable quantities.

Example 17.7

At 298 K, the most probable velocity of an Ar atom is 352.4 m/s. Calculate Λ, the thermal de Broglie wavelength, and the most probable value of λ, the (normal) de Broglie wavelength of an Ar atom. Ar has a molar mass of 39.9 g.

Solution

The most probable value for the de Broglie wavelength is inversely proportional to its momentum. We will have to express the mass of a single Ar atom, in kg units:

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\,\text{J·s}}{\left[\left(39.9\,\frac{\text{g}}{\text{mol}}\right)\left(\frac{1\text{ kg}}{1000\text{ g}}\right)\left(\frac{1\text{ mol}}{6.02 \times 10^{23}}\right)\right] \cdot 352.4\,\frac{\text{m}}{\text{s}}}$$

$$\lambda = 2.8369 \times 10^{-11}\text{ m}$$

Now let us calculate the thermal de Broglie wavelength:

$$\Lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2}$$

$$= \left\{\frac{(6.626 \times 10^{-34}\text{ J·s})^2}{2 \cdot 3.1415926 \cdot \left[\left(39.9\,\frac{\text{g}}{\text{mol}}\right)\left(\frac{1\text{ kg}}{1000\text{ g}}\right)\left(\frac{1\text{ mol}}{6.02 \times 10^{23}}\right)\right] \cdot 1.381 \times 10^{-23}\,\frac{\text{J}}{\text{K}} \cdot 298\text{ K}}\right\}^{1/2}$$

Note that we have again had to determine the mass of a single Ar atom, in kg units. Solving:

$$\Lambda = 1.6005 \times 10^{-11}\text{ m}$$

The two answers are not that far off from each other (in fact, they differ by a factor of $\pi^{1/2}$).

The thermal de Broglie wavelength actually has some utility in a statistical approach to the behavior of matter. In order for the equations of the Boltzmann distribution to apply to a system, it is necessary that the thermal de Broglie wavelength be much, much smaller than the distance between the particles. If this is so, then the thermal de Broglie wavelength of any two particles is negligible compared to their separation, and the individual gas particles can be considered truly independent of each other. Therefore, conditions of low pressure and high temperature—both of which contribute to an increased interatomic separation—are desirable when comparing theory with experiment. We will see examples of how naive predictions of statistical thermodynamics do not agree with experiment at particularly low absolute temperatures in the next chapter.

17.8 Summary

The mathematics of statistics are applicable to atoms and molecules, as we have seen by applying statistical math to a monatomic gas. By considering how many ways we can distribute energy among many gas particles that are distributed into an ensemble (a canonical ensemble, in particular), it becomes clear that the overall properties of the gas can be understood if we know the properties on only one distribution, the most probable distribution. This understanding leads to an expression for the partition function. Using the statistical mathematics of averages, we can express measurables like energy and entropy in terms of that partition function. The partition function, q, thus becomes the central focus of our understanding of the statistical nature of thermodynamics.

Quantum mechanics and calculus allows us to determine an explicit expression for q for the three-dimensional motion of the gas particles. Using that expression, we can determine expressions for E (called U in phenomenological thermo), H, and heat capacities. The true test, however, is S: we know absolute values of S experimentally, so a comparison of S values determined experimentally with those calculated using statistical thermodynamics is crucial. Table 17.1 shows that the equations derived from a statistical approach to thermo passed the test.

Boltzmann's derivations depended on the existence of matter being, ultimately, particulate. This is consistent with modern atomic theory. Boltzmann's ideas—including the idea that atoms behave statistically—have been accepted as a correct understanding of matter.

17.2 Statistics

17.1. How many ways are there of putting three identical balls in four separate boxes, with one ball in each box? Does the number of possibilities agree with equation 17.1? How many different ways are there if there are no restrictions on the number of balls in each box?

17.2. How many different ways are there of putting a red, a blue, and a green ball in four separate boxes? Compare your answer with exercise 17.1.

17.3. Estimate the value of 1,000,000! (that is, one million factorial). Express your answer in terms of a power of 10 as well as a power of *e*.

17.4. One form of Stirling's approximation is $N! = (2\pi)^{1/2}N^{N+1/2}e^{-N}$. Show that equation 17.2 can be obtained from this.

17.5. An even more exact form of Stirling's approximation is

$$(N-1)! = e^{-N}\cdot N^{N-1/2}\cdot(2\pi)^{1/2}\cdot\left(1+\frac{1}{12N}+\frac{1}{288N^2}+\cdots\right)$$

where higher-order terms inside the parentheses are omitted. Take the natural logarithm of this expression and evaluate ln (5000!). Compare your answer with the value given in the table below equation 17.2. How close are the different values?

17.6. Determine the average score on an exam two different ways and show that the same average score is obtained. The scores are 78, 44, 74, 92, 85, 50, 74, 80, 80, and 90.

17.7. For values of some observable that can be represented by a function, the average value of that observable is the area under that function (that is, the integral) divided by the interval. Population densities of insects can often be expressed as a function. Assume that in the first month of a calendar year interval, two insects are released into a controlled system. As the year progresses, they have some offspring, which in turn have some offspring, until by the middle of the year there are 38 insects in the system. Then as the year progresses, insects die off and at the beginning of the next calendar year there are only two left. Plotting the number of insects versus the month, it is found that the population follows the quadratic equation

$$\text{No. of insects} = -(7-x)^2 + 38$$

where *x* is the number of the month in the year (starting with 1). Determine the average number of insects per month in the system.

17.8. If the n_i values are all the same, a shorthand way of indicating a combination is $C(x, y)$, which is read, "How many combinations are there of *x* distinguishable objects separated into systems, each of which have *y* things?" Evaluate **(a)** $C(10, 2)$ **(b)** $C(3, 1)$ **(c)** $C(6, 3)$ **(d)** $C(6, 2)$. (*Hint:* you should determine the number of systems you need for each case first.)

17.3 & 17.4 Ensembles; Most Probable Distribution

17.9. A grand canonical ensemble is defined as an ensemble whose microsystems all have the same volume, temperature, and chemical potential. Rewrite equations 17.4–17.6 to relate the states of the microsystems with the state of the overall system.

17.10. Redo exercise 17.9, except for a microcanonical ensemble. The definition of the microcanonical ensemble is in the text.

17.11. What is the most probable distribution of a three-particle system having four possible energy levels, as shown in Figure 17.5, where the system has a total of 5 energy units? Are the thermodynamic properties of such a system determined solely by considering that most probable distribution? Why or why not?

17.12. A common thought experiment is to suppose that all of the gas molecules in a room may instantaneously cluster in one corner of the room, killing everyone in the room. Explain in statistical thermodynamic terms why we don't need to worry about this ever happening.

17.13. The derivation of equation 17.15, in which derivatives are applied to a summation and only a single term remains as a more simplified expression, is best illustrated by example. A function Φ can be expressed in terms of three variables, ξ_1, ξ_2, and ξ_3 as

$$\Phi = \sum_{i=1}^{3} C_i\xi_i$$

where the C_i values are the coefficients multiplying each variable ξ.

(a) Write the expression for Φ explicitly (that is, without the summation sign) and verify that $\partial\Phi/\partial\xi_1 = C_1$, $\partial\Phi/\partial\xi_2 = C_2$, and $\partial\Phi/\partial\xi_3 = C_3$.

(b) Write a general expression for the derivative of Φ with respect to ξ_i, in which *i* can be either 1, 2, or 3. Compare this general expression with equation 17.15 and explain how equation 17.15 was derived from the expression immediately preceding it.

17.14. Explain why *q* is a constant for a given system at a specified temperature.

17.15. What is the ratio of ground-state nickel atoms (in which *E* is defined as zero) to nickel atoms that are in the first excited state of 200 cm^{-1} at 298 K? (The spectrum of Ni atoms is complicated by the existence of such an excited state. Does your answer explain why?) Assume the two states have the same degeneracies.

17.16. Using the fact that $\beta = 1/kT$, show that equations 17.29 and 17.30 are equivalent.

17.17. What temperature is necessary to have twice as many atoms in the ground state as in the first excited state, at 16.4 cm^{-1}, of C atoms? What temperature is necessary to have equal populations in the ground state and the second excited state, at 43.5 cm^{-1}? What temperature is necessary to have equal populations in the first and second excited states? The degeneracies of the ground, first, and second excited states are 1, 3, and 5, respectively. (Note that these equilibrium ratios would not be possible at any temperature if the degeneracies were equal.)

17.5 Thermodynamic Properties

17.18. Several times it has been mentioned that q is a constant, but the expression for energy (as well as many other thermodynamic functions) contains the derivative of q (or the derivative of ln q). The derivatives of constants are zero. Why aren't thermodynamic state functions equal to zero, then?

17.19. **(a)** On the basis of their statistical thermodynamic definition, which energy has the higher absolute value, A or G? **(b)** On the basis of their statistical thermodynamic definition, can you tell which energy has the higher absolute value, E or G? Why or why not?

17.20. By following the steps outlined in the text, derive equation 17.42 from equation 17.41.

17.21. For a chemical system with more than one component, what is the restriction on the derivation of equation 17.46?

17.22. Derive equations 17.44 and 17.45.

17.23. Use statistical thermodynamic arguments to justify the second-law spontaneity of the following situations. **(a)** A gas expands as the volume of a system increases adiabatically. **(b)** Ice is the unstable phase of H_2O at 5°C.

17.24. Equations 17.44 and 17.45 for A and G differ only by the $+1$ term in the definition of A. Where does this term come from? (See exercise 17.22 above.)

17.25. Using L'Hôpital's rule, determine the limit of S as $T \rightarrow 0$ and show that it equals $k \ln g_0$.

17.6 & 17.7 Monatomic Gases and State Functions

17.26. Do a strict units analysis of equation 17.53 by breaking down all the units of all the quantities into their basic units and show that they all cancel.

17.27. What change is there in the Sackur-Tetrode equation if $N = N_A$?

17.28. In calculating thermodynamic properties for 1 mole of a monatomic gas, we use the mass of a single atom, not the mass of a mole of atoms. Explain why.

17.29. Verify equation 17.56, starting with equation 17.34.

17.30. Derive the Sackur-Tetrode equation, equation 17.61.

17.31. Calculate the thermal de Broglie wavelength of He at 25 K and 500 K. Are the different values to be expected?

17.32. Explain why the calculated value for the absolute entropy of Kr at 120 K might not be very close to the experimental value, even though the boiling point of Kr is 119.8 K.

17.33. Calculate S for **(a)** C atoms at 1000 K, **(b)** Fe atoms at 3500 K, and **(c)** Hg atoms at 298 K. Compare your calculated values to 183.2, 239.6, and 174.9 J/(mol·K), respectively. Assume 1 atm pressure. Can you explain the trend in agreement between calculation and experiment?

17.34. Use equation 17.56 to determine the change in energy, ΔE, when 1 mole of Ar is heated from 298 K to 348 K at constant volume. Compare this result with the change in energy calculated using (mass)(specific heat)(change in temperature). You will need to look up the specific heat of argon; see the table of thermodynamic values in Appendix 2.

17.35. For an electron that has a velocity of $0.01c$ (where c is the speed of light), at what temperature will its thermal de Broglie wavelength equal its quantum-mechanical de Broglie wavelength? (Note that the original de Broglie wavelength is not directly dependent on temperature.)

17.36. Use the Sackur-Tetrode equation to derive the relationship $\Delta S = R \ln (V_2/V_1)$ for an isothermal change and $\Delta S = C_V \ln (T_2/T_1)$ for an isochoric change.

Symbolic Math Exercises

17.37. Calculate the logarithm of $N!$, $N = 1$ to 100, explicitly and using Stirling's approximation, and compare the values. At what approximate value of N does Stirling's approximation agree with the true value to within 1%?

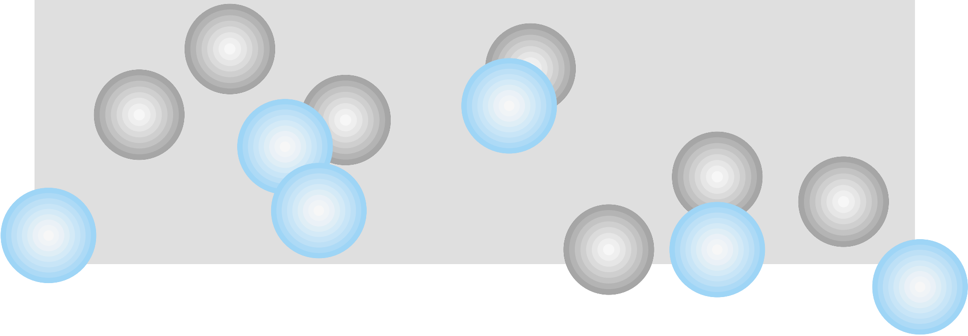
17.38. Consider a system of five energy levels, each of which are doubly degenerate. The levels have energies of 0, 1×10^{-21}, 2.5×10^{-21}, 4×10^{-21}, and 6×10^{-21} J. Calculate the partition function of this system at 50, 100, 200, 300, 500, and 1000 K. Do you see a leveling off of the value of q as the temperature increases? What is the interpretation of the values of q?

17.39. Use a symbolic math program to take the symbolic limit of equation 17.52 as n approaches infinity, and compare the result to equation 17.54.

17.40. Program the Sackur-Tetrode equation, 17.61, into a calculator or computer and calculate the molar entropy of all noble gases at 298 and 1000 K.

18

More Statistical Thermodynamics



THE PREVIOUS CHAPTER INTRODUCED some of the basic concepts that led to the development of a statistical approach to energy and entropy. This is statistical thermodynamics. By the end of the chapter, equations were applied to monatomic gases, and thermodynamic state functions—mostly entropy—were calculated whose values were very close to experimental values. Also, in some of the exercises you were asked to derive some simple expressions that were also derived from phenomenological thermodynamics. For example, we know from early chapters in this book that the equation $\Delta S = R \ln (V_2/V_1)$ is applicable for an isothermal change in volume of an ideal gas. We can also get this expression using the Sackur-Tetrode statistical thermodynamic expression for S. These correspondences are just two examples where phenomenological and statistical thermodynamics are consistent with each other. That is, they ultimately make the same predictions about the state functions of a system, and how they change with a process.

We will see more examples of such correspondence in the current chapter, because we are going to expand our application of statistical thermodynamics to include molecules in the gas phase. (We will still be considering the gas phase almost exclusively.) Recall that we established the partition function, q, as a central figure in the equations of statistical thermodynamics. Also, remember that q was originally defined as (and ultimately remains) a summation of negative exponentials involving the energy levels that the gas particles of a microstate can occupy. For atomic gas particles, the energy levels were limited to translational states, since we ignored electronic and nuclear energy levels. We will consider the latter two in this chapter, and make the case that in most (but not all) systems, these energy levels contribute little to the overall q.

But molecules have other energy states that atoms don't. They have rotational and vibrational energy states that can have an important impact on q. Indeed, we found in our discussion of rotational spectroscopy that molecules occupy excited (that is, $J > 0$) rotational energy levels at normal temperatures! This suggests, correctly, that the existence of such energy levels has an impact on q, and correspondingly on the thermodynamic properties of molecular gases.

Once we establish the complete partition function of a molecular gaseous species, we will consider one additional application of the partition function: the chemical change. In the last chapter, a few exercises asked for a determination of the Δ(something) of a physical process, like the expansion of a monatomic gas. However, in chemistry we are often concerned with the change in the *chemical* identity of a species—a chemical reaction. It may surprise you to learn that the partition functions of each chemical species in a balanced chemical reaction can be used to determine a characteristic property of that reaction: its equilibrium constant.

18.1 Synopsis

First, we will define electronic and nuclear parts of the partition function, which were ignored in the previous chapter. It will be demonstrated, though, that for most systems they can be neglected. We also present counterexamples in which the electronic or nuclear partition functions can't be neglected—not to be confusing, but as a lesson that they shouldn't be ignored automatically. In both of these cases, we will find that the partition functions can actually be expressed in terms of the original definition of q. But for the rotational and vibrational partition functions, this is not the case. We will be able to rewrite the infinite summation over the energy levels to get a new expression for q. These expressions will be determined with the help of quantum mechanics and the equations for the quantized energies of an object rotating in three-dimensional space (the 3-D rigid rotor) or vibrating in a Hooke's-law type of oscillation (the harmonic oscillator).

Recognizing that molecules are an important part of chemistry, we will define a molecular partition function, Q, that is the product of partition functions from various energies of a molecule: translational, vibrational, rotational, electronic, and nuclear.

A chemical reaction is a process that we can apply statistical thermodynamics to. The ΔH or ΔS value of a process is determined by the H or S value of the products minus the H or S value of the reactants. In being able to calculate H or S (or any other state function) of product or reactant species, we should be able to calculate the ΔH or ΔS value of the process from a statistical thermodynamic perspective. We will ultimately find that the very concept of an equilibrium constant—that is, that a *constant* defines the long-term extent of any reaction—comes directly from statistical thermodynamics. This, if anything, should establish the impact that a *statistical* approach to atoms and molecules has on our understanding of chemistry.

There was some attempt to extend these ideas to phases other than gases. Historically, some of the most useful extensions were to crystals. We will finish our (nowhere near exhaustive) treatment of "stat thermo" with a discussion of this application. The discussion has its human aspects, because it is an interesting example of a case in which Einstein was wrong. (Or at least, not as "right" as others were.)

18.2 Separating *q*: The Nuclear and Electronic Partition Functions

In the previous chapter, we suggested that the overall partition function q for a monatomic gas is

$$q = q_{\text{trans}} \cdot q_{\text{elect}} \cdot q_{\text{nuc}} \tag{18.1}$$

Further, we approximated $q \approx q_{\text{trans}}$, and were able to determine an expression for q in terms of various quantities, including the masses of the atoms and several universal constants. From that q, we were able to derive expressions for E, S, and related state functions and show that the statistical thermodynamic values for these state functions were very close to experiment (for S) or agreed with the values predicted by other theories (like $E = \frac{3}{2}kT$ for a monatomic gas as predicted by kinetic theory, which we will consider in a later chapter).

Does this imply that q_{trans} is the overwhelming contribution to the overall q and that all other partition functions make negligible contributions? No, not for all gaseous species. This assumption worked well with monatomic gases that have all-electron-paired singlet electronic states, and have no vibrations or rotations (they are, after all, simply atoms). Vibrational and rotational partition functions don't exist for atomic species, and since most of the gases of interest have filled orbitals, no electronic states contribute substantially to the partition function (an issue we will consider in more detail later), and our approximation of $q \approx q_{trans}$ is a very good one.

What about q_{nuc}? What is the contribution of nuclear energy levels to the overall partition function?

From the definition of partition function, q_{nuc} is defined as

$$q_{\text{nuc}} = \sum_{\substack{i=\text{first}\\ \text{nuclear level}}}^{\infty} g_i e^{-\epsilon_i/kT} \tag{18.2}$$

where the summation explicitly states that it is taken over the possible *nuclear* energy levels. Nuclear energy levels are dictated by the arrangement(s) of protons and neutrons in the nucleus. Nuclear energy levels are on the order of millions of electron volts, or 10^{11} joules, per mole! The very idea of nuclear energy, and its immense magnitude with respect to chemical energies, suggests that the spacing of nuclear energy levels is very large, so large that if the first nuclear energy level were arbitrarily set to an energy of zero, equation 18.2 becomes

$$q_{\text{nuc}} = g_1 + \sum_{\substack{i=\text{second}\\ \text{nuclear level}}}^{\infty} g_i e^{-\epsilon_i/kT} \tag{18.3}$$

Note that in equation 18.3, the exponential in the first term is equal to 1, and the summation in equation 18.3 now starts at the *second* nuclear energy level. But if even the second nuclear energy level (that is, the first "nuclear excited state") is so high in energy, the negative exponential in even the first term of the summation is very, very small; successive terms are even smaller. We suggest that the $i = 2$ term, and all higher terms, are so negligible that they can be ignored. The nuclear partition function is therefore

$$q_{\text{nuc}} = g_1 \tag{18.4}$$

That is, the (effective) nuclear partition function is the degeneracy of the ground state of the nucleus.

For chemical purposes, the nuclear partition function is ignored. This is for several reasons. First of all, a degeneracy is likely to be some small whole number. Although this has the overall effect of multiplying the overall q by that whole number, it does not really affect the determination of thermodynamic properties. For one thing, many thermodynamic properties are related to how q changes with temperature or pressure. Because changes in nuclear energy levels are so large, it would take millions or billions of degrees or atmospheres to have any significant change in q_{nuc}. Since chemistry typically doesn't consider such extremes, the effect of q_{nuc} can be safely ignored. Furthermore, for state functions that are directly related to ln q or q, having q_{nuc} as a simple whole number translates to a small additive correction to the overall value of the state function, especially when compared to the contributions of the other q values. Since the correction is relatively small, it can easily be ignored. Also, for changes in state functions, nuclear states are usually not changed, so this very small correction cancels in the final-minus-initial value determination. As such, it never even shows up.

For all these reasons, q_{nuc} is justifiably ignored in chemistry. This reinforces the minimal influence nuclei have on chemistry, which is more the domain of electrons. (However, we will soon consider an interesting—and surprising—effect of nuclear states on chemistry.)

The electronic part of the partition function for an atom (we consider molecules later) is considered similarly to the nuclear partition function, as an explicit summation over the negative exponentials of the electronic energy levels:

$$q_{\text{elect}} = \sum_{\substack{i=\text{first} \\ \text{electronic level}}}^{\infty} g_i e^{-\epsilon_i/kT} \tag{18.5}$$

Again, if we define the zero point for electronic energy as the ground electronic state, equation 18.5 becomes

$$q_{\text{elect}} = g_1 + \sum_{\substack{i=\text{second} \\ \text{electronic level}}}^{\infty} g_i e^{-\epsilon_i/kT} \tag{18.6}$$

In many cases, the terms of the summation can be ignored because, like excited nuclear levels, excited electronic states are so high in energy compared to kT that the negative exponential is a negligible number compared to g_1, the degeneracy of the ground state.

However, this is not always the case. Many systems have low-lying electronic excited states, whose energies above the ground state are not high with respect to kT. Therefore, the negative exponential is not negligible, especially with degeneracy of the electronic state (g_i) as part of that term in the summation. Strictly speaking, electronic partition functions must be considered on an individual basis and term-by-term. Only when additional terms become so small that they are negligible can the summation be stopped, or *truncated*. The following examples illustrate.

Example 18.1

The first five electronic states of the carbon atom are:

State	Energy (cm^{-1})	Energy (J)	Degeneracy
1	0	0	1
2	16.4	3.26×10^{-22}	3
3	43.5	8.64×10^{-22}	5
4	10,194	2.0249×10^{-19}	1
5	21,648	4.3001×10^{-19}	1

Determine the value of the electronic partition function q_{elect} using only the first energy level, then by successively including the second, third, fourth, and fifth energy levels. At what energy level can we truncate the summation for the electronic partition function? Assume standard temperature of 25°C.

Solution

We will evaluate each negative exponential and add successive terms to our previous value for the partition function, and see how much q_{elect} changes. Up to the first term, the partition function is easy: it is simply equal to the degeneracy of the ground electronic state:

$$q_{\text{elect},1} = 1$$

Up to the second term, we need to evaluate one negative exponential. (The exponential function exp, introduced in Chapter 17, is the same as *e* except it allows long or complex exponents to appear in a more legible form.)

$$3 \cdot \exp\left[-\frac{3.26 \times 10^{-22}\ \text{J}}{(1.381 \times 10^{-23}\ \text{J/K})(298\ \text{K})}\right] = 2.77$$

Therefore, to two terms, q_{elect} is

$$q_{\text{elect},2} = 1 + 2.77 = 3.77$$

Notice that the inclusion of just the first excited electronic state almost quadrupled the value for q_{elect}. Including the third term:

$$5 \cdot \exp\left[-\frac{8.64 \times 10^{-22}\ \text{J}}{(1.381 \times 10^{-23}\ \text{J/K})(298\ \text{K})}\right] = 4.05$$

the overall q_{elect} is now $1 + 2.77 + 4.05 = 7.82$. Now, for the fourth state:

$$5 \cdot \exp\left[-\frac{2.0249 \times 10^{-19}\ \text{J}}{(1.381 \times 10^{-23}\ \text{J/K})(298\ \text{K})}\right] = 2.139 \times 10^{-21}$$

which is 21 orders of magnitude smaller than the previous term. We won't even check the last term, because it is obvious that adding this last term to q_{elect} will not substantially change its value. Therefore, we can say that q_{elect} for C is 7.82 and can be calculated using only the first three electronic states.

Of course, the temperature of the system will have an effect on which electronic states will contribute to the electronic partition function. (So will the degeneracy of the state, but it has a smaller potential effect on q_{elect}.) Generally, if the ratio E/T has a value of about 10^{-22} J/K *or larger*, the negative exponential is about 0.0007, which is negligible with respect to 1 (the minimum value of q_{elect}). Usually, these and larger terms can be safely ignored in the calculation of q_{elect}. Otherwise, that particular electronic state should be included explicitly.

Example 18.2

Nickel atoms have a low-lying excited state at about 200 cm^{-1} (3.97×10^{-21} J). Assuming that both electronic states have a degeneracy of 3 and that no additional low-lying excited states contribute significantly to the electronic partition function, calculate q_{elect} at 1000 K.

Solution

Checking quickly, we find that the ratio E/T equals $(3.97 \times 10^{-23}\ \text{J})/(298\ \text{K}) = 1.33 \times 10^{-25}$ J/K, which is smaller than our estimated cutoff value of 10^{-22} J/K, so it will have to be included explicitly in the determination of q_{elect}. Therefore, we have the electronic partition function as the sum of two negative exponentials:

$$q_{\text{elect}} = 3 \cdot \exp\left[-\frac{0\text{ J}}{(1.381 \times 10^{-23}\text{ J/K})(1000\text{ K})}\right] + 3 \cdot \exp\left[-\frac{3.97 \times 10^{-23}\text{ J}}{(1.381 \times 10^{-23}\text{ J/K})(1000\text{ K})}\right]$$

Note that we are defining the energy of the ground state as 0 J. We get

$$q_{\text{elect}} = 3 \cdot 1.000 + 3 \cdot 0.997$$

$$q_{\text{elect}} = 5.991$$

If you were to compare q_{nuc} and q_{elect} with q_{trans} as determined in the previous chapter, you would see that q_{trans} is usually huge compared to q_{nuc} and q_{elect}, often by a dozen orders of magnitude or more. This suggests that q_{nuc} and q_{elect} have a very small impact on the overall thermodynamic properties of gaseous species. This is in fact the case. We have already mentioned how we can virtually neglect q_{nuc} ; as you might expect, in many cases we can virtually neglect the contribution of q_{elect} as well. The exception to this is for molecules that have a large number of low-lying excited states that might have a large degeneracy (for example, they might be very symmetric molecules). And at very high temperatures, low-lying electronic states can contribute significantly to q_{elect}. Generally speaking, it is a good idea to evaluate each system and its relative characteristics before determining q_{elect}. We will see shortly how much q_{elect} affects the calculated values of thermodynamic state functions.

18.3 Molecules: Electronic Partition Functions

We explicitly excluded molecules in our earlier treatment of the electronic partition function. Let us consider q_{elect} for molecules now, starting with a diatomic molecule and generalizing the result to other molecules.

The key to getting an electronic partition function for molecules depends on how we define the "zero" position for energy. Virtually all numerical scales have benchmarks that are used to define certain numerical values. For example, for atoms we defined the zero point as the ground electronic state. Vibrations and rotations have well-defined minimum-energy points that serve as starting points. But what about electronic energy?

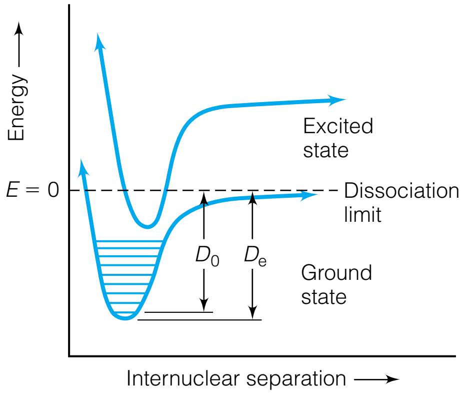


Figure 18.1 The electronic potential energy diagram for a hypothetical diatomic molecule. In the ground state, some of the lower vibrational energy levels are indicated. How is the "zero" point of energy defined for a molecule that has electronic energy with this behavior?

Keep in mind, also, that the electronic potential energy curve isn't just a given, specific value. Because all molecules are constantly vibrating, even in their lowest-energy state, the electronic energy curve is shaped like a (harmonic-oscillator) potential energy curve. Figure 18.1 shows a representative curve for a ground electronic and first excited electronic state of a typical diatomic molecule. In the ground electronic state, the energy is at a minimum at some equilibrium distance labeled r_e. At very small internuclear distances, the potential energy increases as internuclear repulsion becomes strong. At long internuclear distances, the bond between the two atoms will become nonexistent and the molecule will actually exist as two separated atoms. This point is known as the *dissociation limit* for the molecule.

The depth of the electronic potential energy well is called the *dissociation energy*. However, there are two ways to define a dissociation energy. The energy difference between the dissociation limit and the very bottom of the electronic potential well is labeled D_e. However, in reality a molecule will also be in its (presumably) lowest vibrational energy state, which has some nonzero minimum energy. That zero-point energy is $\frac{1}{2}h\nu$, where ν is the classical vibrational frequency of the diatomic molecule. The difference between the dissociation limit and the ground-vibrational state of the electronic potential energy well is labeled D_0. Thus, the relationship between D_e and D_0 is

$$D_e = D_0 + \tfrac{1}{2}h\nu \tag{18.7}$$

We will be using the D_e-defined value for the dissociation energy. However, many tables list D_0, so it is important to keep track of which value is being reported. Equation 18.7 can be used to go from one definition to the other. Both values for dissociation energy are typically given as positive numbers, with D_0 having the slightly smaller magnitude. Values are also usually given in terms of kilojoules per mole of molecules. Remember that in partition functions, values for *individual molecules* must be used.

For q_{elect} of diatomic molecules, the benchmark for electronic energy is the dissociation limit. This means that the dissociation limit is arbitrarily assigned a value of zero energy. At the minimum of the potential energy surface, the electronic energy of the molecule is therefore $-D_e$. (It is negative because it is going *lower* in energy. Also, in this case D_e is the energy needed for *one molecule,* not one mole of molecules.) Using the explicit definition of q, we have

$$q_{\text{elect}} = g_1 e^{D_e/kT} + g_2 e^{-\epsilon_2/kT} + g_3 e^{-\epsilon_3/kT} + \cdots$$

Because D_e is typically large and is a *positive* exponential, the first term in the equation above typically dominates, and we can approximate the diatomic molecule's electronic partition function as

$$q_{\text{elect}} \approx g_1 e^{D_e/kT} \tag{18.8}$$

However, if there are low-lying excited states, the explicit summation definition for q_{elect} must be evaluated, keeping in mind that the zero point for electronic energy is the dissociation limit of the molecule in its ground electronic state.

Example 18.3

The hydrogen molecule has a D_0 of 432 kJ/mol and a vibrational frequency of $1.295 \times 10^{14}\ \text{s}^{-1}$. Calculate H_2's electronic partition function at 298 K. Assume that the ground electronic state is singly degenerate. Hydrogen's first excited electronic state lies $\sim 1.822 \times 10^{-19}$ J above the ground state and has a degeneracy of 1.

Solution

Because we are given D_0, we will have to calculate D_e. Using equation 18.7, we have

$$D_e = \frac{432\ \text{kJ}}{\text{mol}} \cdot \frac{1000\ \text{J}}{1\ \text{kJ}} \cdot \frac{1\ \text{mol}}{6.02 \times 10^{23}\ \text{molecules}} + \frac{1}{2}(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})(1.295 \times 10^{14}\ \text{s}^{-1})$$

In the first term, we have converted D_0 into number of joules per molecule. Solving:

$$D_e = 7.61 \times 10^{-19}\ \text{J}$$

Now, calculating the electronic partition function:

$$q_{\text{elect}} = 1 \cdot \exp\left[\frac{7.61 \times 10^{-19}\ \text{J}}{(1.381 \times 10^{-23}\ \text{J/K})(298\ \text{K})}\right]$$

$$q_{\text{elect}} = 2.03 \times 10^{80}$$

Let us check to see if we need to include any contribution of the first excited state to the value of q_{elect}. Since the D_e for H_2 is 7.61×10^{-19} J, the minimum on the potential energy curve for the ground electronic state lies at -7.61×10^{-19} J with respect to the zero point, and there is an excited electronic state 1.822×10^{-19} J above that. Therefore, with respect to the zero point of energy, ϵ_2 has a value of $(-7.61 \times 10^{-19} + 1.822 \times 10^{-19})$ J, or -5.79×10^{-19} J. (It might be useful to draw some electronic potential energy curves to verify this.) Evaluation of $g_2 e^{-\epsilon_2/kT}$ gives us

$$g_2 \cdot \exp\left(-\frac{\epsilon_2}{kT}\right) = 1 \cdot \exp\left[-\frac{(-5.79 \times 10^{-19}\ \text{J})}{(1.381 \times 10^{-23}\ \text{J/K})(298\ \text{K})}\right]$$

$$= 1.26 \times 10^{61}$$

Granted, this is a large number, but it is still 19 orders of magnitude smaller than the first term, and is negligible with respect to the first term in q_{elect}. Thus, it can be ignored, as can the contribution of any additional excited electronic states.

Since q_{elect} is so large, what effect does it have on thermodynamic state functions? Actually, very little at normal temperatures. The large values of q_{elect} are just a consequence of where the zero point of energy was selected. For state functions that are related to the derivative of q with respect to temperature and pressure, q_{elect} changes only very, very slowly with changes in temperature and pressure for most systems. Therefore, its effect on state functions is small. For A and G, which depend directly on q, the practical effect is small because we are mostly interested in *changes* in A and G, and the direct numerical consequences of q_{elect} cancel. The translational partition function still has the majority of influence—but not all, as we will see—on the thermodynamic properties of diatomic molecules.

Finally, we should generalize q_{elect} for larger molecules. The issue is the same: what is the zero point against which the electronic energy is measured? For multiatomic molecules, the zero point of electronic energy is defined in the same way as for diatomics: the energy where all atoms are separated (technically, to an infinite distance) from each other. Similar to the dissociation energy, the *atomization energy* is defined as the difference between this separation of atoms and the ground electronic state of the molecule. All other treatment of q_{elect} for molecules is as previously discussed for diatomics.

18.4 Molecules: Vibrations

In order to complete the definition of the partition function for molecules, we must consider the two other ways a molecule can have energy. It can have rotational energy, and it can have vibrational energy.

Molecules are composed of multiple atoms that are bonded by covalent bonds. Quantum mechanics indicates that those atoms are constantly vibrating about some equilibrium position, even at absolute zero, having some nonzero minimum energy of vibration (the "zero-point energy"). Because vibrational motions of molecules represent another form of energy, we can define a vibrational partition function q_{vib} for a molecule such that

$$q_{\text{vib}} = \sum_{\substack{i=\text{first}\\ \text{vibrational level}}}^{\infty} g_i e^{-\epsilon_i/kT} \tag{18.9}$$

(Vibrational energy levels do not exist for monatomic gaseous species, because at least two atoms must be bonded together in order to have a vibration.)

We will consider a simple diatomic molecule first, then generalize our final equations for a polyatomic molecule that has $3N - 6$ (or $3N - 5$ for linear molecules) vibrational motions, where N is the number of atoms in the molecule. If we make the assumption that the single vibration of a diatomic molecule is an ideal harmonic oscillator, then quantum mechanics gives us an equation for the quantized energy of that harmonic oscillator:

$$E = h\nu(v + \tfrac{1}{2}) \tag{18.10}$$

where E is the energy of the harmonic oscillator, h is Planck's constant, ν is the classical frequency of the oscillator, and v is the vibrational quantum number. The classical frequency ν can be expressed as

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{18.11}$$

where k is the force constant of the oscillator (in units of N/m) and μ is the reduced mass of the oscillator (in units of kg). Finally, recall that for a diatomic molecule having two atoms with masses m_1 and m_2, the definition of reduced mass is

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2} \tag{18.12}$$

which can also be written as

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \tag{18.13}$$

Having re-established the definitions of the terms in equation 18.10, we will use that equation to rewrite our vibrational partition function. Making the substitution for ϵ_i in equation 18.9:

$$q_{\text{vib}} = \sum_{\substack{i=\text{first}\\ \text{vibrational level}}}^{\infty} g_i \cdot \exp\left[-\frac{h\nu(v_i + \frac{1}{2})}{kT}\right] \tag{18.14}$$

Here, we are using the summation index i as the index on the quantum number v. Because of the sum of two terms in the power of the exponential, we can rewrite equation 18.14 as

$$q_{\text{vib}} = \sum_{\substack{i=\text{first}\\ \text{vibrational level}}}^{\infty} g_i \cdot \exp\left(-\frac{v_i h\nu}{kT}\right) \cdot \exp\left(-\frac{\frac{1}{2}h\nu}{kT}\right) \tag{18.15}$$

The $\exp(-\frac{1}{2}h\nu/kT)$ part is the same for all of the infinite terms in the summation.* Therefore, we can factor it out of the summation (and make the $\frac{1}{2}$ term

---

*Of course, for real molecules the vibrational quantum number never reaches infinity. However, the final expressions still do a remarkable job of predicting thermodynamic properties for molecules.

a 2 in the denominator of the exponent) and assume that each vibrational level is singly degenerate so that g_i equals 1:

$$q_{\text{vib}} = e^{-h\nu/2kT}\left(\sum_{\substack{i=\text{first}\\ \text{vibrational level}}}^{\infty} e^{-v_i h\nu/kT}\right) \tag{18.16}$$

There is no need to approximate the infinite sum in equation 18.16 as an integral, for it turns out that the summation is a well-known infinite sum that converges to a known value: $(1 - e^{-h\nu/kT})^{-1}$. We can substitute for the summation and get as an expression for q_{vib}:

$$q_{\text{vib}} = e^{-h\nu/2kT}(1 - e^{-h\nu/kT})^{-1} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} \tag{18.17}$$

This expression is applicable at any temperature.

There are several ways we can deal with equation 18.17. The first thing to point out is that in order for the exponent in the exponentials to be unitless, the expression $h\nu/k$ must have units of temperature, kelvins. We define the *vibrational temperature* of a diatomic molecule, θ_{v}, as

$$\theta_{\text{v}} \equiv \frac{h\nu}{k} \tag{18.18}$$

Equation 18.17 can be rewritten as

$$q_{\text{vib}} = \frac{e^{-\theta_{\text{v}}/2T}}{1 - e^{-\theta_{\text{v}}/T}} \tag{18.19}$$

Additionally, in the limit of high temperature (and by high we mean at least well above the vibrational temperature θ_{v}), the exponentials in equation 18.19 have small exponents. Under these conditions, exponentials can be approximated by the Taylor-series expansion

$$e^x \approx 1 + x + \frac{x^2}{4} + \cdots$$

Truncating at the second term, we have for equation 18.19:

$$q_{\text{vib}} = \frac{1 - \theta_{\text{v}}/2T}{1 - (1 - \theta_{\text{v}}/T)}$$

At high temperatures, the $\theta_{\text{v}}/2T$ term is negligible with respect to 1 and is ignored in the numerator, and in the denominator the 1's cancel. We get

$$q_{\text{vib}} = \frac{1}{\theta_{\text{v}}/T}$$

This is usually rewritten as

$$q_{\text{vib}} = \frac{T}{\theta_{\text{v}}} = \frac{kT}{h\nu} \quad (\text{at high } T) \tag{18.20}$$

This is an extremely simple expression for a partition function. Table 18.1 lists a few θ_{v} values for some diatomic molecules. At temperatures well above θ_{v} for each gas-phase molecule, the vibrational partition function is given simply by equation 18.20. At temperatures near θ_{v} or lower, the more complete expression in equation 18.19 must be used. (But be careful: for some of the molecules listed, the stable phase is not the gas phase at $T < \theta_{\text{v}}$!)

Table 18.1 Vibrational temperatures θ_{v} for some diatomic molecules

Molecule	θ_{v} (K)
H_2	6215
HCl	4227
CO	3100
N_2	3374
HBr	3700
Cl_2	810
NO	2690
I_2	310
O_2	2230
HI	3200

Example 18.4

For I_2 (g), θ_v is 310 K. Calculate q_{vib} for I_2 at the following temperatures:
a. 30 K
b. 1000 K

Solution

a. At 30 K, we should probably be using the more explicit expression for q_{vib}, since we are well below the vibrational temperature. Therefore we would have

$$q_{vib} = \frac{\exp\left[-\frac{310\text{ K}}{2(30\text{ K})}\right]}{1 - \exp\left(-\frac{310\text{ K}}{30\text{ K}}\right)}$$

Evaluating, we have

$$q_{vib} = 5.70 \times 10^{-3}$$

b. At 1000 K, we are above the vibrational temperature, so we can use the abbreviated expression for q_{vib}. Therefore we have

$$q_{vib} = \frac{1000\text{ K}}{310\text{ K}} = 3.23$$

Interestingly, if we use the more explicit definition of q_{vib}, we get $q_{vib} = 3.21$. (Try this yourself and see.) The abbreviated expression for q_{vib} is thus a valid approximation.

Most molecules have more than two atoms, so there are more vibrations than one to consider. In Chapter 14, we found that a molecule that has N atoms will have either $3N - 5$ (for linear molecules; at least one of the vibrations will be doubly degenerate) or $3N - 6$ (for nonlinear molecules) normal vibrations that are used to define its possible vibrational motions. (For simplicity's sake, we assume a nonlinear molecule so we don't have to consider the linear-verus-nonlinear issue at every turn, but you should recognize where the differences will be.) The overall vibrational energy can therefore be separated into $3N - 6$ vibrational parts:

$$E_{vib} = E_{\nu_1} + E_{\nu_2} + E_{\nu_3} + \cdots + E_{\nu_{3N-6}}$$

The subscripts ν_1, ν_2, and so on are the typical labels used to represent the individual normal modes of vibration. The vibrational partition function for a polyatomic, nonlinear molecule is, by substituting into equation 18.9,

$$q_{vib} = \sum_{\substack{i=\text{first}\\ \text{vibrational level}}}^{\infty} g_i \exp\left(-\frac{E_{\nu_1} + E_{\nu_2} + E_{\nu_3} + \cdots + E_{\nu_{3N-6}}}{kT}\right) \quad \textbf{(18.21)}$$

Notice that there are two sums in this expression: a summation over the individual *vibrational modes* (which is the summation in the exponent of the exponential) and a summation over the possible *vibrational levels* (which is the summation indicated by the Σ sign).

As we did before, we can separate the exponential into individual parts. Equation 18.21 can be rewritten as

$$q_{vib} = \left(\sum_{i=1}^{\infty} g_i e^{-E_{\nu_1}/kT}\right)\left(\sum_{i=1}^{\infty} g_i e^{-E_{\nu_2}/kT}\right)\left(\sum_{i=1}^{\infty} g_i e^{-E_{\nu_3}/kT}\right) \cdots$$

up to $3N - 6$ terms. One way of writing this is to use the Π symbol; q_{vib} can be written as

$$q_{\text{vib}} = \prod_{j=1}^{3N-6} \sum_{i=1}^{\infty} g_i e^{-E_{v,j}/kT} \tag{18.22}$$

As complicated as this expression might seem, it is simply the product of $3N - 6$ individual vibrational partition functions. Rather than repeat the derivation of the vibrational partition function, we will simply take the result from the case of the diatomic molecule and state that, for a polyatomic molecule,

$$q_{\text{vib}} = \prod_{j=1}^{3N-6} \frac{e^{-h\nu_j/2kT}}{1 - e^{-h\nu_j/kT}} \tag{18.23}$$

Because we are considering all $3N - 6$ vibrations explicitly, the degeneracies g_i are all 1 and g_i no longer appears in equation 18.23. For molecules, we rarely invoke the high-temperature limit, so equation 18.23 is the preferred expression for q_{vib}. Nonlinear polyatomic molecules have up to $3N - 6$ different vibrational temperatures (there can be fewer independent values of θ_v if the vibrations are doubly or triply degenerate), so in terms of the θ_v values equation 18.23 is

$$q_{\text{vib}} = \prod_{j=1}^{3N-6} \frac{e^{-\theta_{v,j}/2T}}{1 - e^{-\theta_{v,j}/T}} \tag{18.24}$$

Table 18.2 Vibrational temperatures θ_v for some polyatomic molecules

Molecule	θ_v (K) [degeneracy, if $\neq$ 1]
H_2O	2287, 5163, 5350
CO_2	954 [2], 1890, 3360
NH_3	1360, 2330 [2], 4800, 4880 [2]
CH_4	1870 [3], 2180 [2], 4170, 4320 [3]
CCl_4	310 [2], 450 [3], 660, 1120 [3]
NO_2	1900, 1980, 2330

Table 18.2 lists a few vibrational temperatures for some small molecules. Note in equation 18.24 that the vibrational temperatures ($\theta_{v,j}$) have two labels, one to indicate that it is a vibrational temperature, and one to indicate to which vibration of the molecule it refers.

There are two points to consider in light of equation 18.23 or 18.24. First, the more atoms a molecule has, the more terms will be in the product (because as N increases, $3N - 6$ increases). Second, since we should suspect that q_{vib} will have some effect on the thermodynamic properties of the gas, we might also think that as the number of atoms in the molecule increases, the thermodynamic functions will deviate more from monatomic gas thermodynamic values. This is indeed the case, as we will see in a few sections. This is one reason why we confined ourselves to monatomic gases as examples in our earlier treatments. This is also a reason why it was difficult to classically predict thermodynamic properties of molecules: molecules have other ways to distribute energy. This can have a major impact on their thermodynamic properties.

Example 18.5

Determine q_{vib} for H_2O at 298 K, given that its normal modes of vibration are 3720, 3590, and 1590 cm^{-1}. Rationalize whether or not the high-temperature expression for q_{vib} can be used. Assume all frequencies are singly degenerate.

Solution

The first thing to do is to calculate the three θ_v values for H_2O. We use the definition of θ_v in equation 18.18, and recognize the fact that we need to express the three vibrational frequencies in units of s^{-1}. Using h and c appropriately, we find that the three vibrational frequencies are 1.115×10^{14}, 1.076×10^{14}, and $4.767 \times 10^{13}\ \text{s}^{-1}$, respectively. Now, using equation 18.18,

$$\theta_{v,1} = \frac{(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})(1.115 \times 10^{14}\ \text{s}^{-1})}{1.381 \times 10^{-23}\text{J/K}} = 5350\ \text{K}$$

Similarly, the other two vibrational temperatures are 5163 K and 2287 K. All three θ_v values are larger than the stated temperature (298 K), so the high-temperature expression for q_{vib} should *not* be used. We thus calculate the vibrational partition function using equation 18.24. For this molecule, $3N - 6 = 3$, so there will be three terms in the product for q_{vib}:

$$q_{vib} = \frac{\exp\left(-\frac{5350\ \text{K}}{2 \cdot 298\ \text{K}}\right)}{1 - \exp\left(-\frac{5350\ \text{K}}{298\ \text{K}}\right)} \frac{\exp\left(-\frac{5163\ \text{K}}{2 \cdot 298\ \text{K}}\right)}{1 - \exp\left(-\frac{5163\ \text{K}}{298\ \text{K}}\right)} \frac{\exp\left(-\frac{2287\ \text{K}}{2 \cdot 298\ \text{K}}\right)}{1 - \exp\left(-\frac{2287\ \text{K}}{298\ \text{K}}\right)}$$

$$q_{vib} = (0.0001263)(0.0001729)(0.02156) = 4.7081 \times 10^{-10}$$

In the above example, the individual vibration's contribution to the q_{vib} of the molecule was given to illustrate a point. Note that the lower θ_v value's contribution to q_{vib} is two orders of magnitude larger than that of the two higher θ_v values. Because of the negative exponential definition of q_{vib}, lower-frequency vibrations have a proportionately larger effect on q_{vib}. One way to consider this in terms of a Boltzmann distribution is that the lower-frequency (and therefore lower-energy) vibrations are more easily populated thermally.

18.5 Diatomic Molecules: Rotations

Gas molecules also rotate in three-dimensional space, and quantum mechanics says that rotational energies are also quantized. Therefore, we can also consider a q_{rot} part of the complete partition function of a molecule. Since this is the last kind of partition function we define, we will suggest that there is a complete *molecular partition function* Q defined as

$$Q = q_{trans} \cdot q_{elect} \cdot q_{vib} \cdot q_{rot} \cdot q_{nuc} \tag{18.25}$$

in which the complete molecular partition function is represented by the capital letter Q and the individually defined partition functions are represented by the lowercase q's. We will consider Q further in the next section.

Before we can consider the complete molecular partition function Q, we need to know what q_{rot} is. By now you may realize that the basic definition of q_{rot} would be

$$\mathrm{q}_{rot} = \sum_{\substack{i=\text{first}\\ \text{rotational level}}}^{\infty} g_i e^{\epsilon_i/kT} \tag{18.26}$$

in which g_i is the degeneracy of the *i*th rotational level and ϵ_i is the energy of the *i*th rotational level.

The energies of rotation of gas-phase molecules can be approximated very well by the three-dimensional rigid rotor ideal system. In fact, we used this approximation in Chapter 14 to derive a basic understanding of rotational spectroscopy. We can apply that understanding to the rotational energy levels and the rotational partition function. It is easiest to start with the simplest molecule, a diatomic molecule. Furthermore, we will assume that the molecule is heteronuclear; that is, there are two different atoms in the molecule. (We will consider homonuclear diatomic molecules separately, as there are some subtle but interesting differences.)

In Chapter 14, we found that the rotational energy of a diatomic molecule is

$$E_{\text{rot}} = \frac{J(J + 1)\hbar^2}{2I} \qquad \textbf{(18.27)}$$

where J is the rotational quantum number, I is the moment of inertia, and $\hbar$ is Planck's constant divided by 2π. In addition, we found that the Jth rotational state has a degeneracy of $2J + 1$, from the possible values of the z component of the total angular momentum. Using this in equation 18.26, the rotational partition function becomes

$$q_{\text{rot}} = \sum_{\substack{i=\text{first} \\ \text{rotational level}}}^{\infty} (2J + 1) \cdot \exp\left[-\frac{J(J + 1)\hbar^2/2I}{kT}\right]$$

which can be written as

$$q_{\text{rot}} = \sum_{\substack{i=\text{first} \\ \text{rotational level}}}^{\infty} (2J + 1) \cdot \exp\left[-\frac{J(J + 1)\hbar^2}{2IkT}\right]$$

where we have rearranged the exponent in the second expression. Like we did with the expression for the vibrational partition function, we recognize that all of the constants except T (and the rotational quantum number J) in the exponent must collectively combine to yield a temperature unit, so that the overall exponent is unitless. Therefore, we can define the following *rotational temperature* θ_r:

$$\theta_r \equiv \frac{\hbar^2}{2Ik} \qquad \textbf{(18.28)}$$

and replace the group of constants with θ_r:

$$q_{\text{rot}} = \sum_{\substack{i=\text{first} \\ \text{rotational level}}}^{\infty} (2J + 1) \cdot e^{-J(J+1)\theta_r/T}$$

(A diatomic molecule has only one defined rotation and so has only a single θ_r.) At high temperatures, the fraction θ_r/T is small and successive terms in the summation are close to each other. We can again substitute an integral for the summation:

$$q_{\text{rot}} = \int_{J=0}^{\infty} (2J + 1) \cdot e^{-J(J+1)\theta_r/T}\, dJ \qquad \textbf{(18.29)}$$

where J, the rotational quantum number, is the variable.

This integral may seem problematic because of the presence of J in the body of the integral as well as the exponent. But note that in the exponent of the exponential, the expression $J(J + 1)$ can be written as $J^2 + J$. The derivative of $J^2 + J$ is $2J + 1$. We can perform a classic substitution. Let

$$x = J^2 + J$$

$$dx = (2J + 1)\, dJ$$

Now substitute: if we rewrite equation 18.29 as

$$q_{\text{rot}} = \int_{J=0}^{\infty} e^{-J(J+1)\theta_r/T}[(2J + 1)\, dJ]$$

we get

$$q_{\text{rot}} = \int_{x=0}^{\infty} e^{-x\theta_r/T}\, dx \qquad \textbf{(18.30)}$$

Table 18.3 Rotational temperatures θ_r for some diatomic molecules

Molecule	θ_r (K)
H_2	85.4
N_2	2.86
O_2	2.07
Cl_2	0.346
Br_2	0.116
HCl	15.2
HBr	12.1
HI	9.0
CO	2.77
NO	2.42

(Note that the limits on the integral stay the same.) The integral in equation 18.30 has a known solution; it has the form $\int_0^\infty e^{-ax}\,dx = 1/a$. Using this solution, we get

$$q_{\text{rot}} = \frac{T}{\theta_r} = \frac{8\pi^2 IkT}{h^2} \tag{18.31}$$

where the definition of $\hbar$ has been used. Equation 18.31 is applicable only if the temperature of the gas is well above the rotational temperature of the molecule. If this is so, then the rotational partition function of the heteronuclear diatomic gas is easy to calculate. Table 18.3 lists several θ_r values for some heteronuclear diatomic molecules. If the temperature is not obviously higher than θ_r, then equation 18.31 is not applicable, and an explicit summation using equation 18.26 is necessary to calculate q_{rot}. Given the low values of θ_r for most molecules (H_2 is a notable exception), the high-temperature expression for q_r can be used at most temperatures.

Example 18.6

Given that the moment of inertia of hydrogen iodide, HI, is 4.269×10^{-47} kg·m², calculate θ_r and q_{rot} at 310 K. Comment on the units of θ_r.

Solution

Using the definition of θ_r, we have

$$\theta_r = \frac{(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})^2}{(2\pi)^2 \cdot 2 \cdot (4.269 \times 10^{-47}\ \text{kg}\cdot\text{m}^2)(1.381 \times 10^{-23}\ \text{J/K})}$$

The $(2\pi)^2$ term comes from the $\hbar^2$ term in the numerator. One of the joule units cancels directly, and using the fact that $\text{J} = \text{kg}\cdot\text{m}^2/\text{s}^2$, we see that the second joule unit cancels the s^2 unit in the numerator and the $\text{kg}\cdot\text{m}^2$ unit in the denominator. The only remaining unit, K in the denominator of the denominator, comes up to the numerator. We have

$$\theta_r = 9.431\ \text{K}$$

The final unit of kelvins is appropriate for a rotational temperature. The q_{rot} is therefore

$$q_{\text{rot}} = \frac{310\ \text{K}}{9.431\ \text{K}} = 32.9$$

Again, notice that the partition function is a pure number without units, as it is supposed to be.

For a *homonuclear* diatomic molecule, there are additional concerns because we now have identical nuclei. These concerns have to do with the Pauli principle, which was introduced in Chapter 12. Recall that the strict form of the Pauli principle required that a wavefunction of fermions must be antisymmetric with respect to exchange of two identical particles, and that a wavefunction of bosons must be symmetric with respect to exchange of two identical particles. In Chapter 12, we were considering only the electronic wavefunction, so the antisymmetry requirement was stressed. However, in our consideration of an overall molecular wavefunction, we are now including other particles: the nuclei of the atoms. Therefore, we must apply the Pauli principle to other parts of the (homonuclear diatomic) molecule and see how that affects the number of possible wavefunctions (that is, the degeneracies), and thus the partition function. Ultimately, we will see effects on the thermodynamic properties of homonuclear diatomic gases that are caused directly by restrictions of the Pauli principle.

Recall that we defined the overall molecular partition function as

$$Q = q_{\text{trans}} \cdot q_{\text{elect}} \cdot q_{\text{vib}} \cdot q_{\text{rot}} \cdot q_{\text{nuc}}$$

We also separate the overall wavefunction of a molecule into similar parts:

$$\Psi_{\text{total}} = \Psi_{\text{trans}} \cdot \Psi_{\text{elect}} \cdot \Psi_{\text{vib}} \cdot \Psi_{\text{rot}} \cdot \Psi_{\text{nuc}}$$

Of the five parts of Ψ, Ψ_{trans} and Ψ_{vib} can always be considered symmetric as far as the Pauli principle is concerned (no matter which type of particle—a fermion or a boson—the nucleus is). The electronic wavefunction Ψ_{elect} is almost always symmetric. For homonuclear diatomic molecules, there is usually a + superscript on the term symbol of the ground electronic state that implies symmetric behavior; however, some diatomic molecules—O_2 is the noteworthy one—have a superscript minus $(-)$ in their term symbol, indicating that the ground electronic state is actually antisymmetric. Ignoring these rare exceptions (but see the end-of-chapter exercises), ultimately the Ψ_{rot} and the Ψ_{nuc} partition functions combine to determine the overall symmetry of Q for the molecule.

If the nuclei of the atoms in the diatomic molecule have integer spins, they are bosons and the complete wavefunction (translational-nuclear-vibrational-electronic-rotational) *must* be symmetric with respect to exchange. If the nuclei of the atoms in the diatomic molecule have half-integer spins, then they are fermions and the complete wavefunction *must* be antisymmetric upon exchange. Given that Ψ_{trans} and Ψ_{vib} are symmetric and Ψ_{elect} is almost always symmetric for homonuclear diatomic molecules, the overall wavefunction symmetry behavior dictates what combinations of Ψ_{rot} and Ψ_{nuc} are allowed. What we find ultimately is that the combinations of Ψ_{rot} and Ψ_{nuc} have different degeneracies, so that the populations of molecules in various rotational states are skewed from normal expectations.

Nuclei are fermions or bosons depending on whether their spins are half-integers or integers. For a nucleus that has a spin of magnitude I, there are $2I + 1$ possible spin states (just as there are $2J + 1$ possible rotational states). For *two* nuclei, there are $(2I + 1)(2I + 1) = (2I + 1)^2$ possible combinations. Some of these combinations will be symmetric, and some will be antisymmetric. (This is analogous to the consideration of symmetric and antisymmetric electron spin states for the He atom in Chapter 12.) It turns out that for all nuclei, boson or fermion, there are $2I^2 + I$ antisymmetric spin states, and the remaining states [out of the $(2I + 1)^2$ states] are symmetric.

Finally, we note that Ψ_{rot} is symmetric for even values of the J rotational quantum number, and is antisymmetric for odd values of the J rotational quantum number.

We therefore have the following two scenarios:

Scenario 1: boson nuclei (that is, integer spin nuclei)

$$\begin{array}{cccccccccccc}
\Psi_{\text{tot}} & = & \Psi_{\text{trans}} & \times & \Psi_{\text{vib}} & \times & \Psi_{\text{elect}} & \times & \Psi_{\text{nuc}} & \times & \Psi_{\text{rot}} \\
\text{sym} & & \text{sym} & & \text{sym} & & \text{sym}^{*} & & \text{sym} & & \text{sym, } J \text{ even} \\
 & & & & & & & & \text{degen: } (I + 1)(2I + 1) & & \text{degen: } 2J + 1 \\
 & & & & & & & & & \textit{or} & \\
 & & & & & & & & \text{antisym} & & \text{antisym, } J \text{ odd} \\
 & & & & & & & & \text{degen: } 2I^2 + I & & \text{degen: } 2J + 1
\end{array}$$

Scenario 2: fermion nuclei (that is, half-integer spin nuclei)

Ψ_{tot}	$= \Psi_{trans} \times$	$\Psi_{vib} \times$	$\Psi_{elect} \times$	Ψ_{nuc}	$\times$	Ψ_{rot}
antisym	sym	sym	sym*	sym		sym, J odd
				degen: $(I+1)(2I+1)$		degen: $2J+1$
					or	
				antisym		sym, J even
				degen: $2I^2 + I$		degen: $2J+1$

The * on Ψ_{elect} serves as a reminder that in some cases the electronic state may be antisymmetric. Although the degeneracies of the symmetric and antisymmetric nuclear wavefunctions are the same for fermions and bosons, they are not equal to each other. This means that a different number of possible total wavefunctions are available for the homonuclear diatomic molecules, and this will affect the number of molecules occupying each rotational state! Understand what the above scenarios imply. If a molecule has a fermion as a nucleus, then symmetric nuclear states will exist only for odd values of the J rotational quantum number. Similarly, if the nuclei are in an antisymmetric spin state, the molecules will exist only with symmetric rotational states, that is, even values of the J rotational quantum number.

What this does is skew the "normal" population of measured rotational states for homonuclear diatomic molecules, because the degeneracies are different. In fact, in spectra of homonuclear diatomic molecules—and also any linear molecule that is symmetric with respect to a plane perpendicular to the molecular axis, like C_2H_2—there is a profound intensity alternation because of the different populations of odd and even rotational states, based on the above analysis. Figure 18.2 shows a spectrum in which the intensity pattern shows such behavior. This is one of the more spectacular experimental verifications of the Pauli principle.

Example 18.7

Diatomic hydrogen has nuclei with a spin of $\frac{1}{2}$. What would be the expected ratio of molecules in odd rotational states to molecules in even rotational states?

Solution

With a spin of $\frac{1}{2}$, hydrogen's nuclei are fermions. Therefore, according to scenario 2 above, there will be $(I + 1)(2I + 1) = (\frac{1}{2} + 1)(2 \cdot \frac{1}{2} + 1) = 3$

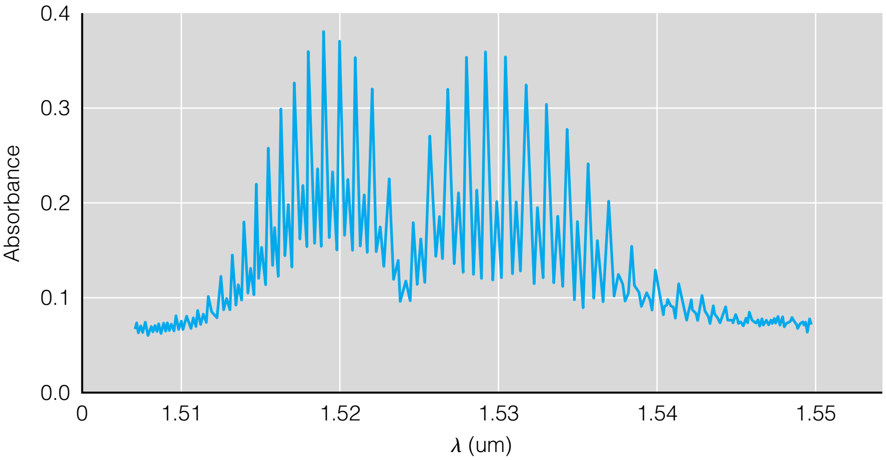


Figure 18.2 This vibrational spectrum of acetylene, C_2H_2, shows intensity variations that are due to the effect of the nuclear wavefunction's symmetry on the degeneracies of the overall wavefunction of the molecule. This is one of the few direct consequences of *nuclear* wavefunctions in chemistry. *Source:* L. W. Richards, *J. Chem. Ed.,* 1996, 43: 645.

symmetric nuclear wavefunctions and $2I^2 + I = 2(\frac{1}{2})^2 + \frac{1}{2} = 1$ antisymmetric nuclear wavefunction. Since all rotational states have the same degeneracy, $2J + 1$, there will be roughly three times as many H_2 molecules in odd rotational states as there are H_2 molecules in even rotational states.

The choice of hydrogen as an example is not random. Because hydrogen's rotational temperature is much higher than its boiling point, hydrogen exhibits unusual thermodynamic properties at low temperatures. This is caused by an extremely slow conversion between symmetric and antisymmetric nuclear states, which effectively limits the transitions between adjacent rotational states. In fact, diatomic hydrogen with the antisymmetric nuclear state is called *para-hydrogen,* and diatomic hydrogen with the symmetric nuclear state is called *ortho-hydrogen.* Ortho- and para-hydrogen have different thermodynamic properties at low temperatures as a consequence of the population differences of the rotational levels, and can effectively behave as two different substances. (For details, consult a statistical thermodynamics textbook.)

For homonuclear diatomic molecules, then, the nuclear and rotational partition functions must be considered together. The only real difference is that the nuclear partition function introduces an additional degeneracy to the overall partition function. Therefore, we have

For boson nuclei:

$$q_{\text{rot,nuc}} = (2I^2 + I)\sum_{J=\text{odd}} (2J+1)e^{-J(J+1)\theta_r/T} + (I+1)(2I+1)\sum_{J=\text{even}} (2J+1)e^{-J(J+1)\theta_r/T}$$

For fermion nuclei:

$$q_{\text{rot,nuc}} = (2I^2 + I)\sum_{J=\text{even}} (2J+1)e^{-J(J+1)\theta_r/T} + (I+1)(2I+1)\sum_{J=\text{odd}} (2J+1)e^{-J(J+1)\theta_r/T}$$

Notice that the only difference between the two partition functions is the index on the summations. For boson nuclei, odd J values have a certain nuclear degeneracy and even J values have another; for fermion nuclei, the nuclear degeneracies are switched.

In the limit of high temperature ($T \gg \theta_r$), we recognize that the summation over even J values is approximately the same as the summation over odd J values, so we can rewrite both equations above as

$$q_{\text{rot,nuc}} = (2I^2 + \text{I})\sum_{\substack{\text{half of}\\ \text{the } J\text{'s}}} (2J+1)e^{-J(J+1)\theta_r/T} + (I+1)(2I+1)\sum_{\substack{\text{half of}\\ \text{the } J\text{'s}}} (2J+1)e^{-J(J+1)\theta_r/T}$$

and we can factor out the summation from both of the terms:

$$q_{\text{rot,nuc}} = (2I^2 + I) + (I+1)(2I+1)\left[\sum_{\substack{\text{half of}\\ \text{the } J\text{'s}}} (2J+1)e^{-J(J+1)\theta_r/T}\right]$$

which can be simplified to

$$q_{\text{rot,nuc}} = (2I+1)^2 \cdot \left[\sum_{\substack{\text{half of}\\ \text{the } J\text{'s}}} (2J+1)e^{-J(J+1)\theta_r/T}\right]$$

The summation over half of the J values is equal to one-half of the summation over all of the J values, so we can substitute $\frac{1}{2}$ times the summation over all J's:

$$q_{\text{rot,nuc}} = (2I + 1)^2 \cdot \tfrac{1}{2} \cdot \sum_{\text{all } J\text{'s}} (2J + 1)e^{-J(J+1)\theta_r/T}$$

Now we can replace the summation with an integral, and perform the same simplification of the integral as we did for a heteronuclear diatomic molecule. We get

$$q_{\text{rot,nuc}} = (2I + 1)^2 \cdot \frac{1}{2} \cdot \frac{T}{\theta_r} = \frac{(2I + 1)^2 \cdot \text{T}}{2\theta_r} \tag{18.32}$$

as the high-temperature limit. This can be separated, approximately, as

$$q_{\text{nuc}} = (2I + 1)^2 \tag{18.33}$$

$$q_{\text{rot}} = \frac{T}{2\theta_r} \tag{18.34}$$

for homonuclear diatomic molecules. Notice what the additional symmetry (that is, a plane of symmetry bisecting the molecule) of the homonuclear diatomic molecules does to q_{rot}: it introduces a factor of 2 in the denominator of the partition function. The factor 2 is called a *symmetry number*. Symmetry numbers also appear in rotational partition functions of polyatomic molecules. Table 18.3 lists some rotational temperatures for homonuclear diatomic molecules.

18.6 Polyatomic Molecules: Rotations

In most cases, for polyatomic molecules the nuclear partition function is again neglected, since it usually has a very small effect on the overall thermodynamic properties of polyatomic molecules. (Indeed, the only reason why we had to consider it for diatomic molecules is because it imposes an obvious, measurable effect on various observations, like spectra and thermodynamic properties to be considered in section 18.8.) In the high-temperature limit, a linear polyatomic molecule has the same rotational partition function as a homonuclear diatomic molecule:

$$q_{\text{rot}} = \frac{T}{\sigma\theta_r}$$

where σ is the symmetry number, which is 1 for nonsymmetric linear molecules (like OCS) and 2 for symmetric linear molecules (like C_2H_2). This expression is essentially the same as equation 18.34 (except for the presence of σ), and ultimately comes from the fact that a linear molecule has only one defined rotational moment of inertia.

A nonlinear polyatomic molecule can have up to three different moments of inertia, labeled I_A, I_B, and I_C. By convention, I_A is less than I_B, which is less than I_C. Polyatomic molecules that have some symmetry may have some of their moments of inertia equal. If all three are equal, then the molecule is called a *spherical top* (see Chapter 14) and the rotational partition function can be written as

$$q_{\text{rot}} = \frac{1}{\sigma} \cdot \sum_{J=1}^{\infty} (2J + 1)^2 \exp\left[-\frac{J(J + 1)\hbar^2}{2IkT}\right] \tag{18.35}$$

where the rotational degeneracy for a spherical top is $(2J + 1)^2$ (for reasons we won't go into). The symmetry number σ is ultimately equal to the number of pure rotational symmetry operations in the point group of the molecule. In our discussions, symmetry numbers will be given in all examples. In the limit of high energies, which imply high J values, the "+ 1" in the degeneracy is negligible and the summation can be replaced with an integral. We therefore have

$$q_{\text{rot}} = \frac{1}{\sigma}\int_0^\infty 4J^2 \cdot \exp\left[-\frac{J(J+1)\hbar^2}{2IkT}\right] dJ$$

This integral has a known solution, and in terms of the variables in the above expression, the high-temperature limit for q_{rot} of a spherical top becomes

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma}\left(\frac{2IkT}{\hbar^2}\right)^{3/2} \tag{18.36}$$

If we define the rotational temperature θ_r for a spherical-top polyatomic molecule as

$$\theta_r \equiv \frac{2Ik}{\hbar^2} \tag{18.37}$$

we have

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma}\left(\frac{T}{\theta_r}\right)^{3/2} \tag{18.38}$$

Although the mathematical processes for symmetric tops and asymmetric tops are less straightforward, the ultimate expressions for the rotational partition functions are variants of equation 18.36 (or 18.38). For a symmetric top, two of the three moments of inertia are equal. The rotational partition function for a symmetric top is

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma}\left(\frac{2I_{\text{duplicate}}kT}{\hbar^2}\right)\left(\frac{2I_{\text{unique}}kT}{\hbar^2}\right)^{1/2} \tag{18.39}$$

In equation 18.39, $I_{\text{duplicate}}$ refers to the two moments of inertia that are equal, and I_{unique} refers to the unique moment of inertia (either I_A or I_C, depending on whether the molecule is a prolate or an oblate top, respectively). Equation 18.39 is applicable to both oblate and prolate tops, with the proper application. For an asymmetric top in which all three moments of inertia are different, we have

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma}\left(\frac{2I_A kT}{\hbar^2}\right)^{1/2}\left(\frac{2I_B kT}{\hbar^2}\right)^{1/2}\left(\frac{2I_C kT}{\hbar^2}\right)^{1/2} \tag{18.40}$$

where I_A, I_B, and I_C represent the three different moments of inertia. In terms of rotational temperatures, equations 18.39 and 18.40 can be written as

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma}\left(\frac{T}{\theta_{r,A}}\right)\left(\frac{T}{\theta_{r,C}}\right)^{1/2} \tag{18.41}$$

for a symmetric top. For an asymmetric top:

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma}\left(\frac{T}{\theta_{r,A}}\right)^{1/2}\left(\frac{T}{\theta_{r,B}}\right)^{1/2}\left(\frac{T}{\theta_{r,C}}\right)^{1/2} \tag{18.42}$$

$$= \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\theta_{r,A}\cdot\theta_{r,B}\cdot\theta_{r,C}}\right)^{1/2}$$

Table 18.4 lists rotational constants and symmetry numbers for some molecules.

Table 18.4 Rotational temperatures θ_r for some polyatomic molecules

Molecule (symmetry number)	θ_r (K)
H_2O ($\sigma = 2$)	13.4, 20.9, 40.1
CO_2 ($\sigma = 2$)	0.561
NH_3 ($\sigma = 3$)	13.6, 13.6, 8.92
CH_4 ($\sigma = 12$)	7.54
CCl_4 ($\sigma = 12$)	0.0823
NO_2 ($\sigma = 2$)	0.590, 0.624, 11.5

Example 18.8

Calculate the rotational partition function of gaseous NH_3 at 1000 K. The rotational temperatures are 13.6 K, 13.6 K, and 8.92 K. The symmetry number for ammonia is 3.

Solution

Since only two different rotational temperatures are given for ammonia, we conclude that the molecule is a symmetric top. We can use equation 18.41 to determine q_{rot}, and we must take care that the correct rotational temperature goes in the correct term. Since 13.6 K is repeated twice, it is used for $\theta_{\text{r,A}}$. We get

$$q_{\text{rot}} = \frac{\pi^{1/2}}{3}\left(\frac{1000\text{ K}}{13.6\text{ K}}\right)\left(\frac{1000\text{ K}}{8.92\text{ K}}\right)^{1/2}$$

Solving:

$$q_{\text{rot}} = 460$$

Note how all of the units cancel, so that q_{rot} is a pure number.

18.7 The Partition Function of a System

At this point, we have determined the complete partition function Q for a molecule. It is

$$Q = q_{\text{trans}} \cdot q_{\text{elect}} \cdot q_{\text{vib}} \cdot q_{\text{rot}} \cdot q_{\text{nuc}}$$

and all of the parts of Q have been evaluated mathematically. This molecular partition function is strictly applicable to a single molecule. What if we have a system that has many noninteracting molecules?

We start off by suggesting that the total energy of a system is the sum of the individual types of energy a molecule can have: electronic, translational, vibrational, and so on. The total energy of the system is the sum of the energies of the individual particles. Thus, due to the original definition of the partition function, the overall partition function for the system is the *product* of the individual partition functions of N molecules:

$$Q_{\text{sys}} = Q_1 \cdot Q_2 \cdot Q_3 \cdot \cdots \cdot Q_N$$

If the system is composed of only one kind of molecule, then all of the individual Q_i values are the same, and we simply have Q being multiplied by itself N times. To write this another way, we have

$$Q_{\text{sys}} = Q^N$$

However, this doesn't account for the fact that the individual molecules in the system are indistinguishable at the macroscopic level. Recall the examples of the balls in boxes at the beginning of Chapter 17. We found that there were fewer possible unique arrangements when the two balls were the same color. Another way to consider this is that there will be fewer possible arrangements if we cannot tell which gas molecules are which; that is, if they are indistinguishable. (We do know, however, that the molecules are the same compound. We just can't tell, say, one molecule of water apart from any other molecule of water in our system.) Similarly, the above expression for Q_{sys} is overvalued. Statistics can show that the value is too high by a multiplicative factor of $N!$

(N factorial). N, recall, is the number of molecules in the system. For indistinguishable particles, then, the overall partition function for the system is

$$Q_{\text{sys}} = \frac{Q^N}{N!} \tag{18.43}$$

For a molecule, we can substitute for Q in several degrees of complexity:

$$Q_{\text{sys}} = \frac{(q_{\text{trans}} \cdot q_{\text{elect}} \cdot q_{\text{vib}} \cdot q_{\text{rot}} \cdot q_{\text{nuc}})^N}{N!}$$

$$\begin{aligned} Q_{\text{sys}} = \frac{1}{N!} &\times \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \cdot V\right]^N \times \left[\frac{\pi^{1/2}}{\sigma}\left(\frac{2I_{\text{A}}kT}{\hbar^2}\right)^{1/2}\left(\frac{2I_{\text{B}}kT}{\hbar^2}\right)^{1/2}\left(\frac{2I_{\text{C}}kT}{\hbar^2}\right)^{1/2}\right]^N \\ &\times (g_1 e^{D_e/kT})^N \times (g_{1,\text{nuc}})^N \times \left(\prod_{j=1}^{3N^*-6} \frac{e^{-\theta_j/2T}}{1 - e^{-\theta_j/T}}\right)^N \end{aligned} \tag{18.44}$$

(with some substitution for special molecules, like homonuclear diatomic molecules. N^* in the vibrational partition function represents the number of atoms in the molecule, to differentiate it from N, the number of molecules in the system).

Equation 18.44 is certainly complicated. However, we note two things. First, virtually all of the information required to evaluate equation 18.44 for a molecule is available experimentally, mostly using various spectroscopic techniques. Second, because equation 18.44 is independent of the identity of the molecule, it is a relatively simple task to write a computer program to evaluate Q_{sys} for a given system. As we will see in the next section, once we have an expression for Q_{sys}, we will be able to derive expressions for various thermodynamic properties. These expressions can also be evaluated by calculator or computer program. In fact, an important use of these equations of statistical thermodynamics is not to verify that they yield numbers that agree with experiment, but to *predict* the thermodynamic properties at different conditions or for new substances whose thermodynamic properties have not been measured.

18.8 Thermodynamic Properties of Molecules from Q

Recall that the major aim of statistical thermodynamics is to be able to calculate the thermodynamic properties of systems using the mathematics of statistics. It has taken us some time and effort to get to this point, because we first had to determine the forms of the partition functions for a molecule. Having done that now, we can turn our attention to thermodynamic properties.

First, we will state that even though the exact expression for the partition function Q is somewhat expanded from the partition function q for a monatomic gas, the basic relationships between Q and various thermodynamic functions are the same. That is,

$$E = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_V \tag{18.45}$$

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T \tag{18.46}$$

$$H = kT\left[\left(T\frac{\partial \ln Q}{\partial T}\right)_V + 1\right] \tag{18.47}$$

$$S = k\left[T\left(\frac{\partial \ln Q}{\partial T}\right)_V + \ln Q + 1\right] \tag{18.48}$$

$$A = -kT(\ln Q + 1) \tag{18.49}$$

$$G = -kT \ln Q \tag{18.50}$$

Notice that each expression involves the natural logarithm of Q (or a derivative of the natural logarithm of Q). Recall also that Q for a molecule is defined as the product of five independent q's. Logarithms of products can be rewritten as the sum of logarithms of the individual terms in the product; that is,

$$\ln Q = \ln(q_{\text{trans}} \cdot q_{\text{elect}} \cdot q_{\text{vib}} \cdot q_{\text{rot}} \cdot q_{\text{nuc}})$$

$$\ln Q = \ln q_{\text{trans}} + \ln q_{\text{elect}} + \ln q_{\text{vib}} + \ln q_{\text{rot}} + \ln q_{\text{nuc}} \tag{18.51}$$

Equation 18.51 implies that if the partition function Q can be separated into the sum of individual logarithm terms, then the thermodynamic functions in equations 18.45 through 18.50 can also be separated into sums of individual energy, enthalpy, entropy, and so on. For example, we can rewrite the total (that is, internal) energy E as

$$\begin{aligned}
E_{\text{trans}} &= NkT^2\left(\frac{\partial \ln q_{\text{trans}}}{\partial T}\right)_V \\
E_{\text{elect}} &= NkT^2\left(\frac{\partial \ln q_{\text{elect}}}{\partial T}\right)_V \\
E_{\text{vib}} &= NkT^2\left(\frac{\partial \ln q_{\text{vib}}}{\partial T}\right)_V \\
E_{\text{rot}} &= NkT^2\left(\frac{\partial \ln q_{\text{rot}}}{\partial T}\right)_V \\
E_{\text{nuc}} &= NkT^2\left(\frac{\partial \ln q_{\text{nuc}}}{\partial T}\right)_V
\end{aligned} \tag{18.52}$$

so that

$$E = E_{\text{trans}} + E_{\text{elect}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{nuc}} \tag{18.53}$$

and similarly for each of the other thermodynamic functions.

Since we have derived expressions for each of the partition functions of a molecule, we can evaluate the expressions in equations 18.52, and similarly for each of the other thermodynamic functions, for each part of the overall molecular partition function. These expressions are given in Table 18.5. You should be able to derive most of the expressions in Table 18.5 by simply performing the appropriate derivation given in equations 18.52 and the equivalent for the other thermodynamic properties. (Remember that $[(\partial \ln q)/\partial T] = (1/q)(\partial q/\partial T)$.)

Heat capacities are defined in terms of the change in E or H with respect to temperature at constant volume or pressure:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

(Again, remember that we are using the variable E to stand for the internal energy in this chapter.) From Table 18.5, we can take the derivative of each term

Table 18.5 Expressions for the various components of the thermodynamic state functions of molecules[a]

State function	trans	nuc	elect
E	$\frac{3}{2}NkT$	—	$-ND_e$
H	$\frac{5}{2}NkT$	—	$-ND_e + NkT$
G	$-NkT\left[\ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{Ve}{N}\right] + NkT$	—	$-ND_e + NkT$
S	$Nk\left[\ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{Ve^{5/2}}{N}\right]$	—	Nkg_1

State function	vib, diatomic	rot, diatomic
E	$NkT\left(\frac{\theta_v}{2T} + \frac{\theta_v/T}{e^{\theta_v/T} - 1}\right)$	NkT
H	$NkT\left(\frac{\theta_v}{2T} + \frac{\theta_v/T}{e^{\theta_v/T} - 1} + 1\right)$	$2NkT$
G	$NkT\left[\frac{\theta_v}{2T} + \ln(1 - e^{-\theta_v/T}) + 1\right]$	$NkT\left(1 - \ln\frac{T}{\sigma\theta_r}\right)$
S	$Nk\left[\frac{\theta_v/T}{e^{\theta_v/T} - 1} - \ln(1 - e^{-\theta_v/T})\right]$	$Nk\ln\frac{T}{\sigma\theta_r} + Nk$

State function	vib, polyatomic	rot, polyatomic
E	$NkT\sum_{j=1}^{3N^*-6}\left(\frac{\theta_v}{2T} + \frac{\theta_v/T}{e^{\theta_v/T} - 1}\right)^{b}$	$\frac{3}{2}NkT^*$
H	$\left[NkT\sum_{j=1}^{3N^*-6}\left(\frac{\theta_v}{2T} + \frac{\theta_v/T}{e^{\theta_v/T} - 1}\right)\right] + NkT^{b}$	$\frac{5}{2}NkT^*$
G	$\left\{NkT\sum_{j=1}^{3N^*-6}\left[\frac{\theta_v}{2T} + \ln(1 - e^{-\theta_v/T})\right]\right\} + NkT^{b}$	$-NkT\ln\frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\theta_A\theta_B\theta_C}\right)^{1/2} + NkT^*$
S	$Nk\sum_{j=1}^{3N^*-6}\left[\frac{\theta_v/T}{e^{\theta_v/T} - 1} - \ln(1 - e^{-\theta_v/T})\right]^{b}$	$Nk\ln\frac{\pi^{1/2}e^{3/2}}{\sigma}\left(\frac{T^3}{\theta_A\theta_B\theta_C}\right)^{1/2*}$

[a] Translational and electronic contributions are the same for all molecules. Vibrational and rotational contributions depend on whether the molecule is diatomic or polyatomic. N = number of species in the system; N^* = number of atoms in molecule.

[b] Expression is different for linear molecules. Consult the text.

of E with respect to temperature and come up with a simple expression for the heat capacity:

$$C_V = Nk\left[\underbrace{\frac{3}{2}}_{\text{trans}} + \underbrace{\frac{3}{2}}_{\text{rot}} + \underbrace{\sum_{j=1}^{3N^*-6}\left(\frac{\theta_j}{T}\right)^2 \cdot \frac{e^{-\theta_j/T}}{(1 - e^{-\theta_j/T})^2}}_{\text{vib}}\right] \tag{18.54}$$

The origins of each part of the heat capacity have been labeled under each term. The derivative in the definition of C_V converts the product function from the vibrational partition function into a summation of terms. Notice what equation 18.54 implies: translations and rotations contribute the same amount to the heat capacity of a gaseous molecule, and vibrations also contribute. The greater the number of atoms N^* in the molecule, the more vibrations, and so the greater the vibrational contribution to C_V. Such observations are indeed made experimentally. An expression for C_p is left as an exercise.

Example 18.9

Calculate the constant-volume heat capacity of 1 mole of gaseous water at 727°C and 1 bar pressure. Compare this to a value of 33.0 J/(mol·K) at 727°C and about 1 atm pressure (where 1 atm = 1.01325 bar) and comment on the difference.

Solution

The three vibrational temperatures for H_2O are 2287, 5163, and 5350 K. (See Example 18.5.) Our expression for C_V becomes

$$C_V = (6.02 \times 10^{23}\ \text{mol}^{-1})\left(1.381 \times 10^{-23}\,\frac{\text{J}}{\text{K}}\right) \times \left\{\frac{3}{2} + \frac{3}{2} + \left(\frac{2287\ \text{K}}{1000\ \text{K}}\right)^2 \cdot \frac{\exp\left(-\frac{2287\ \text{K}}{1000\ \text{K}}\right)}{\left[1 - \exp\left(-\frac{2287\ \text{K}}{1000\ \text{K}}\right)\right]^2}\right.$$

$$\left. + \left(\frac{5163\ \text{K}}{1000\ \text{K}}\right)^2 \cdot \frac{\exp\left(-\frac{5163\ \text{K}}{1000\ \text{K}}\right)}{\left[1 - \exp\left(\frac{5163\ \text{K}}{1000\ \text{K}}\right)\right]^2} + \left(\frac{5350\ \text{K}}{1000\ \text{K}}\right)^2 \cdot \frac{\exp\left(-\frac{5350\ \text{K}}{1000\ \text{K}}\right)}{\left[1 - \exp\left(\frac{5350\ \text{K}}{1000\ \text{K}}\right)\right]^2}\right\}$$

We get

$$C_V = (8.314\frac{\text{J}}{\text{mol}})(3 + 0.658 + 0.154 + 0.137)$$

$$C_V = 32.8\frac{\text{J}}{\text{mol·K}}$$

This is a very good agreement with experiment! The variance comes from the fact that H_2O is certainly not acting as an ideal gas, even at these temperatures and pressures. At higher temperatures and lower pressures, predicted values are much closer to experiment. Finally, notice how much the vibrations contribute to the heat capacity. The lower-energy vibration, which has the lower value of θ_v, contributes much more than the two higher vibrations combined.

The point of this section is that statistical thermodynamics can derive expressions for thermodynamic properties of molecules. Many computer programs are available that use the expressions in Table 18.5 to calculate thermodynamic properties of molecules, given their energy levels (which can be determined spectroscopically or theoretically). Application of these equations gives the physical chemist a powerful tool for understanding the thermodynamic properties of molecules.

18.9 Equilibria

Classical thermodynamics is very useful when applied to chemical or physical processes that are in a state of equilibrium. How well does statistical thermodynamics apply to equilibrium?

Let us assume a balanced, gas-phase equilibrium:

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D \qquad \textbf{(18.55)}$$

where A and B represent reactants, C and D are the products, and ν_A, ν_B, ν_C, and ν_D are the molar coefficients of the balanced chemical reaction.

Algebraically, we can bring the reactants to the other side of the "equation" and rewrite equation 18.55 as

$$\nu_C\mathrm{C} + \nu_D\mathrm{D} - \nu_A\mathrm{A} - \nu_B\mathrm{B} = 0$$

(It is the convention to subtract the reactants from the products.) In terms of classical thermodynamics, chemical equilibrium is given by equation 5.4, which requires that

$$\sum_{i=1}^{\text{no. of components}} \nu_\mathrm{i} \cdot \mu_\mathrm{i} = 0$$

Using the general equation above, we have for this equilibrium

$$\nu_C\mu_C + \nu_D\mu_D - \nu_A\mu_A - \nu_B\mu_B = 0 \tag{18.56}$$

We would like to substitute for μ_i in the equation above. For a mixture of gases, we will assume that the overall partition function of the system Q_{sys} can be written as the product of the molecular partition functions of each component:

$$Q_{sys} = \prod_{\text{components}} \frac{(Q_i)^{N_i}}{N_i!}$$
$$= \frac{Q_A(N_A, V, T)^{N_A}}{N_A!} \cdot \frac{Q_B(N_B, V, T)^{N_B}}{N_B!} \cdot \frac{Q_C(N_C, V, T)^{N_C}}{N_C!} \cdot \frac{Q_D(N_D, V, T)^{N_D}}{N_D!} \tag{18.57}$$

In this equation, we are labeling each molecular partition function with the label of the relevant component. Also, we are reminded that each component is occupying the same volume and has the same temperature (otherwise the system is not at equilibrium), but that each component has its own characteristic amount N_i at equilibrium. Statistical thermodynamics gives an expression for the chemical potential of a component:

$$\mu_i = -kT \ln \left(\frac{\partial Q}{\partial N_i}\right)_{N_{j\neq i}, V, T} \tag{18.58}$$

where in the case of a multicomponent mixture, the partial derivative is taken with respect to only one component, N_i, and the other components remain as constants. This has the effect of eliminating all other species' partition functions from the evaluation of each particular μ_i. After substituting equation 18.57 into equation 18.58 for each of the four components and applying Stirling's approximation, we have

$$\mu_i \approx -kT \ln \frac{Q_i(V, T)}{N_i} \tag{18.59}$$

where we have dropped the N_A . . ., labels from each Q. Substituting for each μ in equation 18.56, we have

$$\nu_C\left(-kT \ln \frac{Q_C(V,T)}{N_C}\right) + \nu_D\left(-kT \ln \frac{Q_D(V,T)}{N_D}\right) - \nu_A\left(-kT \ln \frac{Q_A(V,T)}{N_A}\right) - \nu_B\left(-kT \ln \frac{Q_B(V,T)}{N_B}\right) = 0$$

The $-kT$ terms cancel to yield

$$\nu_C \ln \frac{Q_C(V,T)}{N_C} + \nu_D \ln \frac{Q_D(V,T)}{N_D} - \nu_A \ln \frac{Q_A(V,T)}{N_A} - \nu_B \ln \frac{Q_B(V,T)}{N_B} = 0$$

We can use the properties of logarithms to take each coefficient ν and make it an exponent inside the logarithm term. Removing the remaining labels from Q for clarity gives

$$\ln\left(\frac{Q_C}{N_C}\right)^{\nu_C} + \ln\left(\frac{Q_D}{N_D}\right)^{\nu_D} - \ln\left(\frac{Q_A}{N_A}\right)^{\nu_A} - \ln\left(\frac{Q_B}{N_B}\right)^{\nu_B} = 0$$

In the next step, we will do two things: bring the A- and B-containing terms to the other side of the equation, and combine the two logarithms on each side into one (using the rule that $\ln a + \ln b = \ln ab$):

$$\ln\left[\left(\frac{Q_C}{N_C}\right)^{\nu_C} \cdot \left(\frac{Q_D}{N_D}\right)^{\nu_D}\right] = \ln\left[\left(\frac{Q_A}{N_A}\right)^{\nu_A} \cdot \left(\frac{Q_B}{N_B}\right)^{\nu_B}\right]$$

If the logarithms of two products are the same (as the above equation indicates), then the arguments of the two individual logarithms are the same. Another way to put this is that we can take the inverse logarithm of both sides of the above equation and still have an equality:

$$\left(\frac{Q_C}{N_C}\right)^{\nu_C} \cdot \left(\frac{Q_D}{N_D}\right)^{\nu_D} = \left(\frac{Q_A}{N_A}\right)^{\nu_A} \cdot \left(\frac{Q_B}{N_B}\right)^{\nu_B} \tag{18.60}$$

At this point, we will rearrange equation 18.60 to bring all of the partition functions Q_i to one side and all of the amounts N_i to the other. The exponents ν_i will appear on both sides (as a consequence of the algebra of exponents). By convention, we will write the expressions with product quantities in numerators and reactant quantities in denominators. We get

$$\frac{(Q_C)^{\nu_C} \cdot (Q_D)^{\nu_D}}{(Q_A)^{\nu_A} \cdot (Q_B)^{\nu_B}} = \frac{(N_C)^{\nu_C} \cdot (N_D)^{\nu_D}}{(N_A)^{\nu_A} \cdot (N_B)^{\nu_B}} \tag{18.61}$$

Consider equation 18.61. The partition functions Q_i are constants that are characteristic of each chemical species, and the coefficients ν_i are characteristic of the balanced chemical reaction. Therefore, the left side of equation 18.61 is some constant that is characteristic of the chemical reaction. Equation 18.61 shows that this characteristic constant is related to the amounts of each chemical species *when the reaction reaches chemical equilibrium*, even though each individual Q_i itself is defined in terms of the molecule, not any extent of reaction! Since the fraction in terms of the Q_i values has a characteristic value, then the fraction in terms of the amounts N_i at equilibrium must also have a characteristic value. This value is called the *equilibrium constant* for the reaction.

For an ideal gas, the partition function Q is a simple function of volume (again, from q_{trans}) times a more complicated function of temperature (from several other q's):

$$Q = f(T) \cdot V$$

It is convenient to divide each molecular Q by volume to get a volume-independent partition function:

$$\frac{Q}{V} = f(T)$$

By substituting this volume-independent partition function into the partition function expression for the equilibrium constant, we can get an equilibrium constant, labeled $K(T)$, which is characteristic of the chemical species in the reaction and dependent solely on T:

$$K(T) \equiv \frac{\left(\frac{Q_C}{V}\right)^{\nu_C} \cdot \left(\frac{Q_D}{V}\right)^{\nu_D}}{\left(\frac{Q_A}{V}\right)^{\nu_A} \cdot \left(\frac{Q_B}{V}\right)^{\nu_B}} \tag{18.62}$$

Equation 18.62 shows that statistical thermodynamics can calculate temperature-dependent equilibrium constants from partition functions. Since the partition functions themselves are ultimately determined from the energy levels of the chemical species, we see once again how a knowledge of energy levels—obtained from spectroscopy—helps us make thermodynamic predictions about chemical reactions.

A word about units is necessary. It is important to keep track of all units in equation 18.62, and when comparing calculated results to experimental ones, units must be consistent. Equation 18.62 is the concentration-based equilibrium constant, K_c. Equilibrium constants can also be expressed in terms of the partial pressures of the gas-phase reactants and products. The pressure-based equilibrium constant, K_p, is related to K_c by the expression

$$K_p = K_c \cdot (kT)^{\Sigma \nu_i} \tag{18.63}$$

where $\Sigma \nu_i$ represents the proper combination of the stoichiometric coefficients of gas-phase substances in the balanced chemical reaction. Remember that ν_i values are positive for products and negative for reactants.

Example 18.10

Of necessity, examples of equation 18.62 must be relatively straightforward. Calculate the equilibrium at 298 K for the reaction

$$H_2 + D_2 \rightleftharpoons 2HD$$

Assume that the electronic and nuclear partition functions cancel. Compare the calculated value with the experimental value of 3.26 (unitless).

Solution

Since $\Sigma\ \nu_i = 2 - 1 - 1 = 0$, $K_p = K_c$ in this case. The remaining three partition functions for each species are calculated as follows:

q	H_2	D_2	HD
trans/V	2.737×10^{30}	7.741×10^{30}	5.028×10^{30}
vib	2.959×10^{-5}	6.283×10^{-4}	1.197×10^{-4}
rot	1.746	3.489	4.656

where q_{trans} has been divided by volume. For H_2 and D_2, the rotational partition functions are scaled by a symmetry number of 2. HD has a symmetry number of 1. We have for the equilibrium constant

$$K(T) = \frac{\left(\dfrac{q_{\text{trans}} \cdot q_{\text{vib}} \cdot q_{\text{rot}}}{V}\right)^2_{\text{HD}}}{\left(\dfrac{q_{\text{trans}} \cdot q_{\text{vib}} \cdot q_{\text{rot}}}{V}\right)_{H_2} \cdot \left(\dfrac{q_{\text{trans}} \cdot q_{\text{vib}} \cdot q_{\text{rot}}}{V}\right)_{D_2}}$$

$$= \frac{(5.028 \times 10^{30} \cdot 1.197 \times 10^{-4} \cdot 4.656)^2}{(2.737 \times 10^{30} \cdot 2.959 \times 10^{-5} \cdot 1.746) \cdot (7.741 \times 10^{30} \cdot 6.283 \times 10^{-4} \cdot 3.489)}$$

Notice that the volume terms cancel out of the expression for $K(T)$. We get

$$K(T) = 3.273$$

This is very close to the experimentally determined value.

Statistical thermodynamics thus provides tools for us to predict equilibrium constants of reactions knowing little other than the energy levels of the equilibrium species. This is a powerful predictive tool, one that chemists use to estimate the equilibrium extent of reactions under conditions that might not be directly measurable.

18.10 Crystals

The success of statistical thermodynamics as applied to gaseous systems inspired scientists to try to apply it to other systems. Some of the more instructive attempts occurred at the beginning of the twentieth century. During this period, scientists made the first in-depth studies of matter at very low temperatures, approaching absolute zero. Hydrogen and helium gases were first liquefied in 1898 and 1908, respectively, and the techniques used to generate such low temperatures were used to cool matter down and investigate its properties.

At such low temperatures, most matter is solid, and the best type of solid sample to study is a crystal. Studies of crystals showed some intriguing thermodynamic behavior. For instance, in the measurement of entropy it was found that absolute entropy approached zero as the temperature approached absolute zero. This is experimental verification of the third law of thermodynamics. But a measurement of the heat capacity of the solid showed something interesting: the heat capacity of the solid approached zero as the temperature approached absolute zero, also. But for virtually all crystalline solids, the heat-capacity-versus-temperature plot took on a similar shape at low temperatures, typified by Figure 18.3: the curves have the distinct shape of a cubic function, that is, $y = x^3$. In this case, the variable is absolute temperature, so experimentally it was found that the constant-volume heat capacity C_V was directly related to T^3:

$$C_V \propto T^3 \tag{18.64}$$

(where ∝ means "directly related" or "proportional to"). How can this behavior be explained?

Scientists attempted to use statistical thermodynamics to understand the heat capacities of crystals at low temperatures. Given the success of statistical thermodynamics to gases, in which gas molecules are indistinguishable and

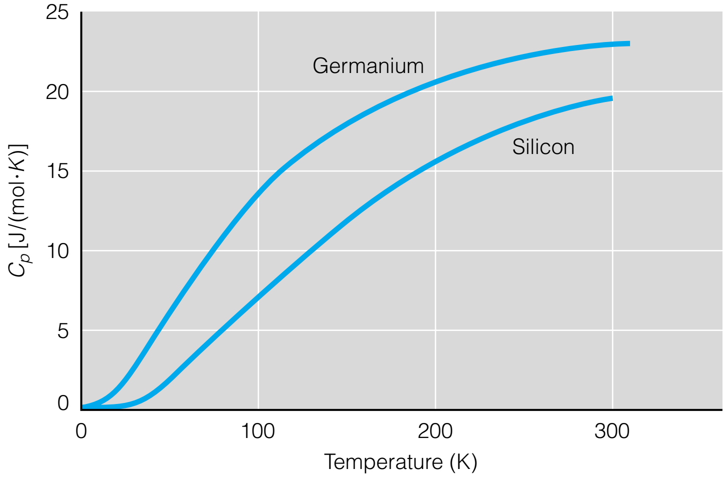


Figure 18.3 Measurement of the heat capacity of crystals at very low temperatures shows a curve that looks like a $y = kT^3$ curve. Any theory of heat capacities of crystals should predict this kind of behavior.

can be treated statistically, why not apply statistical thermodynamics to crystals, whose atomic contributions to the properties of the solid as a whole can probably also be treated statistically?

The first person to make serious headway with this approach was Albert Einstein. In 1907, Einstein proposed to understand the motions of the atoms in the crystal using Planck's idea of quantized energy. A crystal is composed of N atoms, say. These N atoms can vibrate within their crystal lattice in the x, the y, or the z direction, giving a total of $3N$ possible vibrational motions. Einstein assumed that the frequencies of the vibrations were the same, some frequency labeled ν_E, or the *Einstein frequency.* If this were the case, and we are only considering vibration-type motions of the atoms in the crystal, then the heat capacity of the crystal can be determined by applying the *vibrational part only* of the heat capacity from the vibrational partition function:

$$C_V = \sum_{i=1}^{3N} k\left(\frac{h\nu_E}{kT}\right)^2 \cdot \frac{e^{-h\nu_E/kT}}{(1 - e^{-h\nu_E/kT})^2}$$

where we are taking the vibrational component of the heat capacity from equation 18.54 and using the Einstein frequency as the frequency of vibration. Since the Einstein frequency is constant for all $3N$ terms in the sum, the heat capacity becomes

$$C_V = 3Nk\left(\frac{h\nu_E}{kT}\right)^2 \cdot \frac{e^{-h\nu_E/kT}}{(1 - e^{-h\nu_E/kT})^2}$$

As is our habit, we define a temperature

$$\theta_E \equiv \frac{h\nu_E}{k} \tag{18.65}$$

where θ_E is the *Einstein temperature* of the crystal. Einstein's expression for the heat capacity of a crystal is therefore

$$C_V = 3Nk\left(\frac{\theta_E}{T}\right)^2 \cdot \frac{e^{-\theta_E/T}}{(1 - e^{-\theta_E/T})^2} \tag{18.66}$$

Notice how the Einstein temperature and the absolute temperature of the crystal always appear together as the fraction θ_E/T. Notice, too, that there is nothing in equation 18.66 that is sample-dependent other than the Einstein temperature θ_E. This means that if the heat capacity of any crystal were plotted versus θ_E/T, all of the graphs would look exactly the same. This is one example of what is called a *law of corresponding states.* Einstein's derivation of a low-temperature heat capacity of crystals was the first to predict such a relationship for all crystals.

How do we determine the Einstein temperature θ_E without knowing the characteristic "vibrational frequency" of the atoms in the crystal? Typically, experimental data is fitted to the mathematical expression in equation 18.66 and a value of the Einstein temperature is used to allow for the best possible fit to experimental results. For example, a plot of experimental measurements of the heat capacity versus T divided by θ_E (which is proportional to T, whereas θ_E/T is inversely proportional to T and less easy to graph as $T \rightarrow 0$ K) is shown in Figure 18.4. Notice that there is reasonable agreement between experiment and theory, suggesting that Einstein's statistical thermodynamic basis of the heat capacity of crystals has merit. Table 18.6 lists a few experimentally determined Einstein temperatures for crystals.

Table 18.6 Einstein temperatures of various crystals

Material	θ_E (K)
Al	240
C (dia)	1220
Pb	67

However, the Einstein equation deviates from experimental values at very

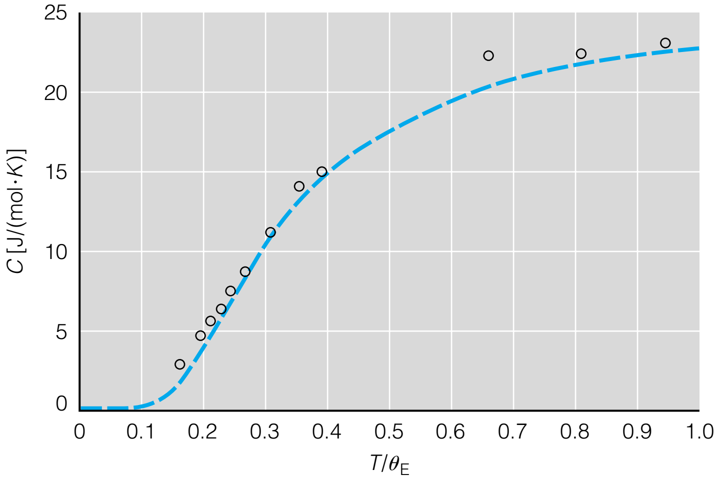


Figure 18.4 The Einstein theory of heat capacity of crystals agrees reasonably well with experimental measurements.

low temperatures, predicting a lower heat capacity than is measured experimentally. In fact, using the mathematics of limits, it can be shown that equation 18.66 predicts the following:

$$\lim_{T\to 0} C_V = 3Nk\left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T} \tag{18.67}$$

This is not the T^3-dependence, as experimental measurements suggest. Therefore, while Einstein's application of statistical thermodynamics to crystals was useful, it has its limitations. (It might be considered similar, in some respects, to Bohr's attempt to describe electron energy levels by assuming quantized angular momentum. It worked in some respects—mostly in application to hydrogen atoms—but had its deficiencies in a more global sense.)

Peter Debye, a Dutch physical chemist after whom the Debye-Hückel theory is partly named (see Figure 18.5), expanded on Einstein's work. Rather than assume that all atoms in a crystal had the same vibrational frequency (as Einstein had presumed), Debye suggested that the possible vibrational motions of the atoms in a crystal could have any frequency from zero to a certain maximum. That is, he suggested that atoms could have a *range,* or *distribution,* of frequencies.

Cornell University, courtesy AIP Emilio Segrè Visual Archives

Figure 18.5 Peter J. W. Debye (1884–1966) was a Dutch-American physical chemist who made important advances in the understanding of ionic solutions and dipoles in molecules. He also formulated an acceptable theory of the thermodynamic properties of crystals at low temperatures. He was awarded the 1936 Nobel Prize in chemistry for his work.

Using an argument similar to that used to determine the number of translational states for q_{trans}, Debye deduced that the equation for the distribution of frequencies, symbolized by $g(\nu)$, is

$$g(\nu)\,d\nu = \frac{9N}{(\nu_D)^3}\cdot \nu^2\,d\nu \tag{18.68}$$

where ν_D is the maximum frequency that the atoms in the crystal can have and is called the *Debye frequency.* The distribution function $g(\nu)$ is a function of the frequencies ν, but is subject to the condition that the total number of vibrations is $3N$, where N is the number of atoms in the crystal. The mathematical way of expressing this restriction is

$$\int_{\nu=0}^{\nu_D} g(\nu)\,d\nu = 3N$$

Equation 18.68 is therefore applicable for values of ν between 0 and ν_D. If ν

were greater than ν_D, $g(\nu) \equiv 0$.

The frequency distribution function in equation 18.68 can be substituted into the statistical thermodynamic expressions for the various state functions, and various thermodynamic properties determined for crystals. We are interested in the expression for the heat capacity. It is (omitting the details of the derivation):

$$C_V = 9Nk\left(\frac{kT}{h\nu_D}\right)^3 \int_0^{h\nu_D/kT} \left(\frac{h}{kT}\right)^5\left(\frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2}\right)\nu^4\,d\nu$$

This is a complicated expression that demands some simplification. First, we substitute for the expression $h\nu/kT$ by defining $x \equiv h\nu/kT$. Second, we define the Debye temperature as

$$\theta_D \equiv \frac{h\nu_D}{k} \quad \textbf{(18.69)}$$

The expression for the heat capacity becomes

$$C_V = 9Nk\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4e^x}{(e^x-1)^2}\,dx \quad \textbf{(18.70)}$$

The integral in equation 18.70 cannot be solved analytically, but its value can be determined numerically. Just like the Einstein treatment of heat capacities of crystals, the Debye temperature θ_D is selected so that the numerical evaluation of equation 18.70 agrees as closely as possible with experimental data. Figure 18.6 shows curve fits of experimental data, and Table 18.7 lists some values of θ_D.

Applying limits to equation 18.70 shows that

$$\lim_{T\to 0} C_V = \frac{12\pi^4}{5}Nk\left(\frac{T}{\theta_D}\right)^3$$

This expression shows that the low-temperature heat capacity varies with the cube of the absolute temperature. This is what is seen experimentally (remember that a major failing of the Einstein treatment was that it didn't predict the proper low-temperature behavior of C_V), so the Debye treatment of the heat

Table 18.7 Debye temperatures of various crystals

Material	θ_D (K)[a]
Al	390
C (dia)	1860
Pb	88
Na	150
Ag	215
Au	170
Fe	420
Pt	225
Gd	169
Sc	345

[a] It can be shown that $\theta_E \approx \frac{3}{4}\theta_D$.

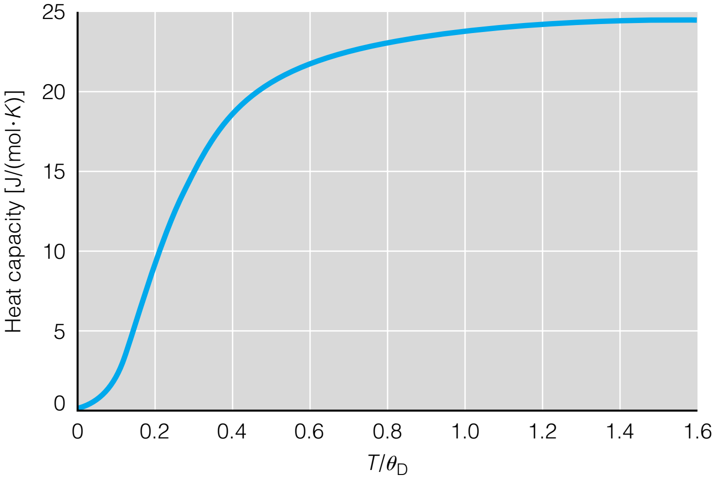


Figure 18.6 The Debye theory of heat capacity of crystals agrees better with experimental values of heat capacity at low temperatures.

capacity of crystals is considered more successful. Once again, because absolute temperature and θ_D always appear together as a ratio, Debye's model of crystals implies a law of corresponding states. A plot of the heat capacity versus T/θ_D should (and does) look virtually identical for all materials.

Both Einstein's and Debye's treatment of crystals are approximations in the sense that they assume some ideal behavior. Like real gases, real solids do not behave ideally. Regardless, application of statistical thermodynamics gives us a starting point for the thermodynamic understanding of these systems, much as the ideal gas law gives us a starting point for understanding the properties of real gases.

18.11 Summary

We have seen how statistical thermodynamics can be applied to systems composed of particles that are more than just a single atom. By applying the partition function concept to electronic, nuclear, vibrational, and rotational energy levels, we were able to determine expressions for the thermodynamic properties of molecules in the gas phase. We were also able to see how statistical thermodynamics applies to chemical reactions, and we found that the concept of an equilibrium constant presents itself in a natural way. Finally, we saw how some statistical thermodynamics is applied to solid systems. Two similar applications of statistical thermodynamics to crystals were presented. Of the two, Einstein's might be easier to follow and introduced some new concepts (like the law of corresponding states), but Debye's agrees better with experimental data.

It was stated at the beginning of the previous chapter that thermodynamics is one topic in which ideas can be developed from two completely different perspectives and arrive at the same conclusions. What these different perspectives guarantee is a wide applicability of thermodynamics to virtually every aspect of chemistry.

EXERCISES FOR CHAPTER 18

18.2 Nuclear and Electronic Partition Functions

18.1. Using a table of nuclear spin states, determine q_{nuc} for **(a)** ^{12}C atoms, **(b)** ^{56}Fe atoms, **(c)** ^{1}H atoms, **(d)** D (D is ^{2}H) atoms. Explain your answers for parts c and d.

18.2. How many terms would you recommend for the summation of the electronic partition function for **(a)** N_2 gas; **(b)** O_2 gas at standard temperature? You may need to consult a table of electronic energy levels (as in G. Herzberg, *Spectra of Diatomic Molecules,* Van Nostrand Reinhold, New York, 1950, or G. Herzberg and K. P. Huber, *Constants of Diatomic Molecules,* Van Nostrand Reinhold, New York, 1979).

18.3. Use equation 18.4 to evaluate the nuclear contributions to E and S. How do you justify the answers you get?

18.4. Repeat Example 18.1, but this time for $T = 10{,}000$ K (a surface temperature of a hot star). Does your conclusion about the effect of electronic excited states on q_{elect} change? Why or why not?

18.5. What is the minimum value of q_{elect}? Why is this so?

18.6. Compare q_{elect} for Ni atoms at 298 K with q_{elect} for Ni atoms at 1000 K (see Example 18.2). Can you explain why they are so close? Now compare q_{elect} for Ni atoms at 5.0 K with q_{elect} at 298 K. Can you explain the difference?

18.3 Molecular Electronic Partition Functions

18.7. The vibrational frequency of H_2 (g) is 4320 cm^{-1}. What is the change in q_{elect} at 298 K for H_2 if D_0 is used as the dissociation energy instead of D_e? The bond energy in H_2 is 432 kJ/mol. Compare your answer with the answer in Example 18.3.

18.8. What is the electronic partition function for H_2O (g) at 373 K if it takes 918 kJ to break both O–H bonds?

18.9. Diatomic helium (He_2) exists only in very low temperature gas samples. Upper limits to its bond energy are estimated at 89.8 J/mol. **(a)** Calculate q_{elect} for He_2 at 4.2 K, the normal boiling point of He. **(b)** Comment on whether or not you would expect He_2 to exist at room temperature (~300 K). Explain your answer.

18.4 Molecular Vibrational Partition Functions

18.10. Consider two identical planets that are the same distance from their star. One planet has an atmosphere of argon gas, and the other has an atmosphere of fluorine gas. Assume that all other physical descriptions of the planets are the same. From statistical thermodynamic perspectives, which planet should have the higher atmospheric temperature? Justify your answer by citing specific equations from the chapter.

18.11. What is the expected ratio of vibrational partition functions for H_2 and D_2? Use the high-temperature form of q_{vib} to estimate your answer.

18.12. Calculate the vibrational partition function for NH_3 (g) at 250 K, 500 K, and 1000 K. Do the changes in q_{vib} show the expected differences? Consult Table 18.2 for necessary information.

18.13. Calculate the vibrational partition function of CH_4 (g) at 298 K. See Table 18.2.

18.14. Use the information in Table 18.2 to calculate the vibrational frequencies of carbon tetrachloride in units of cm^{-1}. How many total vibrational frequencies does CCl_4 have?

18.5 & 18.6 Molecular Rotational Partition Functions

18.15. What are minimum values for q_{nuc} and q_{rot} for a gas-phase molecule? What about q_{vib}?

18.16. Determine the temperature at which q_{rot} for HCl equals the q_{rot} value for HBr at 298 K. See Table 18.3 for necessary data.

18.17. What is the expected ratio of rotational partition functions for H_2 and D_2? Compare this ratio with the answer from exercise 18.11.

18.18. Diatomic oxygen, O_2, has an antisymmetric ground electronic state. If oxygen nuclei are bosons ($I = 0$), what are the expected symmetry pairings of the nuclear and rotational wavefunctions?

18.19. The rovibrational spectrum of acetylene, H–C≡C–H, shows intensity variations consistent with expected nuclear degeneracies. Would you expect D–C≡C–H to show similar intensity variations? Why or why not?

18.20. What happens to θ_r of a diatomic molecule as J increases? Why? (*Hint:* See section 14.5.)

18.21. Determine q_{rot} for NH_3 ($\sigma = 3$) and CCl_4 ($\sigma = 12$) at 298 K. Consult Table 18.4 for the rotational temperatures.

18.7 & 18.8 *Q* and Thermodynamic Properties

18.22. Determine an expression for C_p. (*Hint:* use equations 18.47 and 18.54.)

18.23. Using the expression you determined from the previous exercise, answer this: of the heat capacities C_p and C_V, which is larger? Will this always be the case? Why or why not?

18.24. Use equation 18.46 to show that $pV = NkT$.

18.25. Calculate E, H, G, and S for HCl at standard pressure and 25°C. σ equals 1 for this molecule, and $D_e = 431.6$ kJ/mol.

18.26. Determine E, H, G, and S for CH_4 at standard pressure and 25°C. σ equals 12 for methane and the atomization energy of CH_4 is 1163 kJ/mol. Compare your calculated value of S with the tabulated (that is, experimentally determined) value in Appendix 2.

18.27. Use statistical thermodynamics to determine $\Delta H°(25°C)$ and $\Delta S°(25°C)$ for the reaction

$$H_2\ (g) + D_2\ (g) \longrightarrow 2HD\ (g)$$

You should be able to calculate vibrational and rotational temperatures for D_2 and HD using the values for H_2 and the changes in the reduced masses of the other gaseous species.

18.28. Use statistical thermodynamics to determine $\Delta H°$ and $\Delta S°$ for the reaction

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (g)$$

Compare this with the value of $\Delta_f S°$ for H_2O (g) from Appendix 2. Note the phase label on the product.

18.29. Verify the expressions for E in Table 18.5 (except for vibrations).

18.9 & 18.10 Equilibria and Crystals

18.30. The chapter uses the right side of equation 18.61 to argue that the overall expression must be a constant at equilibrium. Support such an argument using the *left* side of equation 18.61 for a reaction at equilibrium.

18.31. Show that the isotope exchange reaction below should ideally have high-temperature equilibrium constant of 4.

$$^{14}N_2 + {}^{15}N_2 \rightleftharpoons 2\,^{14,15}N_2$$

Assume that the dissociation energies of the molecules are the same.

18.32. Determine the equilibrium constant for the following reaction at 1000 K and 1 atm pressure for each species:

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (g)$$

σ equals 2 for H_2O, H_2, and O_2. $D_e(H_2) = 431.8$ kJ/mol, $D_e(O_2) = 493.7$ kJ/mol, and $D_e(H_2O) = 917.6$ kJ/mol. Compare it with the equilibrium constant at 1000 K determined using classical thermodynamic means (that is, $\Delta G = \Delta H - T\,\Delta S$, with $T = 1000$ K, then find the equilibrium constant K from ΔG) and explain the difference in the equilibrium constants. Which one do you think is closer to the experimental value?

18.33. In Chapters 17 and 18 we have derived expressions for the absolute amounts of the energies H and G. However, in tables of thermodynamic data, we always tabulate ΔH and ΔG (that is, *changes* in enthalpy and Gibbs free energy). How do you explain this apparent discrepancy?

18.34. The Einstein-Debye suggestion that atoms in crystals "vibrate" has some validity. In fact, the vibrations of atoms in solids are treated as if they were caused by real particles called *phonons* that have characteristic vibrational frequencies. For solid Al, the frequency of the phonons is about $4.5 \times 10^{12}\ s^{-1}$. If this phonon were approximated as a stretching type of vibration of a single Al atom, what would be **(a)** the equivalent force constant of this "stretch," and **(b)** the wavenumber of light that this phonon would absorb? **(c)** Many solid materials are very good absorbers of low-energy infrared light. Does your answer to part b agree with this generality?

Symbolic Math Exercises

18.35. The law of Dulong and Petit states that the C_V of materials approaches $3Nk$ (which equals $3R$) at high temperatures. Can you show that both Einstein's and Debye's expressions for the heat capacity of crystals agree with this generalization at high temperatures?

18.36. Diatomic hydrogen has a vibrational frequency of $4320\ cm^{-1}$. Evaluate the vibrational partition function at different temperatures and determine the temperature above which the high-temperature limit for q_{vib}, given by equation 18.20, is valid.

18.37. The rotational temperature of molecular iodine is 310 K. Evaluate q_{rot} at $T = 298$ K term by term, listing the cumulative value of q_{rot} for every term. At what number of terms does the change in q_{rot} become negligible? Repeat the evaluation for $T = 1000$ K.

18.38. Write a set of equations (or a small program) to evaluate the constant-volume heat capacity for a molecule. Use this algorithm to determine the heat capacity versus temperature (say from 298 K to 1000 K) for H_2O and CH_4.

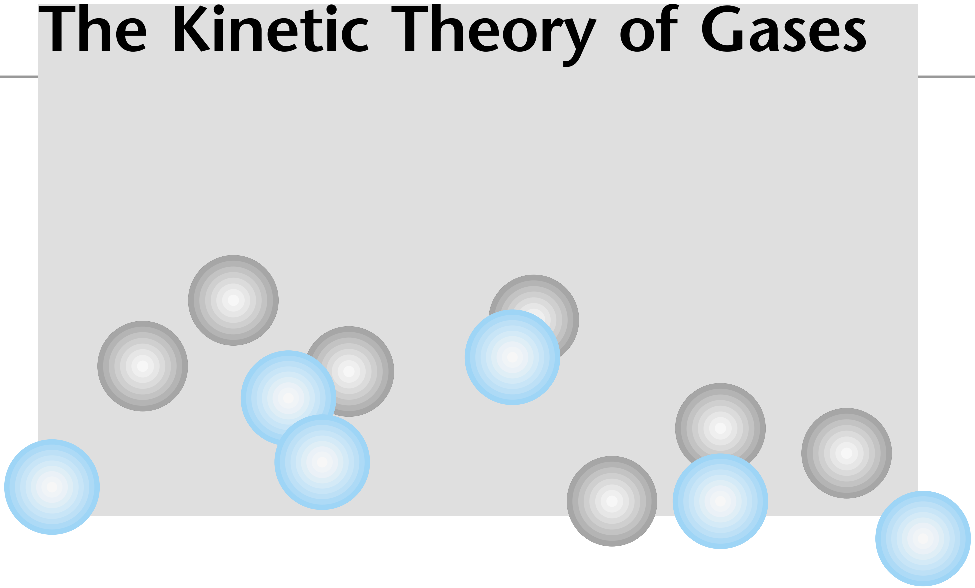
18.39. Silver metal is a very good conductor of heat. The following are heat capacities at different temperatures. Using equation 18.66, determine a value for the Einstein temperature θE that best fits this data.

T (K)	C [J/(g·K)]
1	7.2×10^{-6}
2	2.39×10^{-5}
3	5.95×10^{-5}
4	1.24×10^{-4}
6	3.9×10^{-4}
8	9.1×10^{-4}
10	0.0018
15	0.0064
20	0.0155
25	0.0287
30	0.0442
40	0.078
50	0.108
60	0.133
70	0.151

Source: D. R. Lide, ed., *CRC Handbook of Chemistry and Physics,* 82nd ed., CRC Press, Boca Raton, Fla., 2001.

19

The Kinetic Theory of Gases



WHY DO GASES BEHAVE THE WAY they do? In some of the previous chapters, we have used gases as examples with an implicit understanding that we are modeling their behavior, but we never really got into a discussion of why they have that behavior.

The basic understanding of how gases behave is called the kinetic theory of gases. It is based on several assumptions, mostly related to classical mechanics. In part because of this, most of the basics of the kinetic theory were worked out in the 1860s by Ludwig Boltzmann and James Clerk Maxwell (two names that should be familiar by now). It was the culmination of over two centuries of investigations into the nature of the gas phase, starting with Boyle and continuing through Gay-Lussac, Charles, Amonton, Dalton, and Graham, among others.

In this chapter, we will review the kinetic theory of gases, focusing on ideal gases. This review allows us to revisit some of the topics from Chapter 1 (in which we discussed the nature of gases in a more phenomenological perspective) so that we can better apply these ideas when we consider chemical reactions in the gas phase in the next chapter.

19.1 Synopsis

What we will find in this chapter is that the physical behavior of gases can be understood if some simple assumptions are made. Suppose we treat an individual gas particle as a hard piece of matter: What are the properties of a collection of "hard pieces of matter"? It turns out that we can predict some properties by applying classical, rather than quantum, mechanics. The physical behavior of gases can be considered as a statistical average of all of the individual gas particles, so some of the ideas in this chapter are reminiscent of statistical thermodynamics. In addition, we will be focusing on the physical behavior of gases, not their chemical behavior. Because chemistry depends on electrons, it is vital to understand how electrons behave in order to understand how chemicals behave; that is, we need quantum mechanics. But in order to understand the physical behavior of matter, we are able to use more simple physical theories of nature. Some of these physical behaviors are relevant to chemical behavior, as we will see in chemical kinetics.

In this chapter on kinetic theory, we will consider the origin of the pressure of gases. We will find that the speeds of gas particles can have many values but the distribution of their speeds can be calculated. So can an average speed—in several different ways. We will also consider how many times gas particles collide with each other, how far they travel between collisions, and how far they travel from an arbitrary starting point. One of the more curious things from kinetic theory is the prediction that gas particles are moving very fast indeed, but because of all their collisions their net displacements change rather slowly.

19.2 Postulates and Pressure

The kinetic theory of gases is based on several postulates, or statements that are presumed but not proven. In this respect, it is similar to Dalton's theory of the atomic structure of matter, which is also based on certain presumed statements. The kinetic theory of gases is based on the following statements:

1. Gases are composed of tiny particles of mass.
2. These tiny particles are in constant motion when in the gas phase.
3. These tiny particles do not interact with each other, nor with the walls of the container. That is, there are no forces of attraction or repulsion between any two particles or a particle and the wall. (We will clarify this statement shortly.)
4. These tiny particles do collide with each other and the walls of the container. However, when a collision occurs, the total energy before the collision equals the total energy after the collision. One way of expressing an ideal collision like this is that the total energy is *conserved* (it does not change) and that collisions are *elastic*.

From these statements, the mathematics and predictions of the kinetic theory of gases can be determined.

First, let us address a property commonly measured for a gaseous phase: its *pressure*. This is one of the basic observable properties of a gas. Where does the pressure of a gas come from?

If gas particles are constantly moving (which is the second postulate above), then each gas particle has some kinetic energy. Classically, kinetic energy has the formula

$$\text{kinetic energy} = \tfrac{1}{2}mv^2 \tag{19.1}$$

where m is the mass of the moving body and v is its velocity. Velocity is a vector (although we are not indicating it as such here), and in three dimensions we can separate velocity into its three components v_x, v_y, and v_z. If we do this, equation 19.1 becomes

$$\text{kinetic energy} = \tfrac{1}{2}m(v_x^2 + v_y^2 + v_z^2) \tag{19.2}$$

In a collection of N gas particles in some volume V, each gas particle has its own particular kinetic energy (because we haven't constrained the kinetic energy at all; so far, the kinetic energy of any gas particle could be anything). Therefore, there are N equation 19.2's that when added together give the total kinetic energy of the gas.

As the postulates above mention, the gas particles are constantly moving and, in the course of some of the motions, are colliding with the wall of the container that holds the gas. Figure 19.1 shows a diagram of a single gas particle colliding with the container wall. Before the collision, the particle has

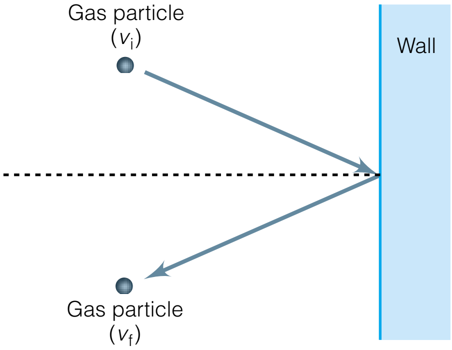


Figure 19.1 A gas particle colliding with the wall of a container. Initially, the particle has velocity v_i. After the collision, the particle has velocity v_f. Even if the magnitude of the velocity has not changed, the gas particle has accelerated because the velocity's direction has changed. Kinetic theory uses this model to understand the pressure of a gas.

some initial velocity labeled v_i, and after the collision it has some final velocity v_f. The change in the velocity, which is a vector quantity, over the period of time it takes for the collision to occur means that the particle has *accelerated.* In terms of the velocities shown in Figure 19.1:

$$\text{acceleration} = \frac{\Delta v}{\Delta t} = \frac{v_f - v_i}{\Delta t}$$

If Figure 19.1 represented the infinitesimal change in velocity, the acceleration would be expressed in derivative form:

$$\text{acceleration} = \frac{dv}{dt}$$

The force involved in the process illustrated by Figure 19.1 is given by Newton's second law:

$$F = ma$$

where F is the force, m is the mass of the object, and a is the acceleration. Using the derivative form for acceleration, this becomes

$$F = m \cdot \frac{dv}{dt} \tag{19.3}$$

for a single particle. Newton's third law says that for every force, there must be an equal and opposite force, so if a gas particle collides with a wall and a force on the particle is produced, an equal (and opposite) force is produced on the wall. F, then, refers to the force on the particle as well as the force on the wall.

In the above expressions, F represents the force exerted by *one* gas particle making *one* collision on the wall of the container. For a macroscopic sample, many gas particles are colliding with the walls of the container over an extended period of time. Therefore, the force on the wall can vary with time, and it is better to consider $F(t)$, force as a function of time. The *average force, F_{avg}*, is the total force over a certain time period divided by the total time period. If we break time into tiny intervals, this becomes

$$F_{avg} = \frac{\displaystyle\sum_{\substack{\text{no. of time}\\ \text{intervals}}} F(t)}{\text{total time}}$$

Of course, if the intervals are so small that they are infinitesimal, then the summation can be replaced with an integral:

$$F_{avg} = \frac{\int F(t)}{\text{total time}} = \frac{1}{\text{time}} \int F(t)\ dt$$

We can substitute from equation 19.3 to get

$$F_{avg} = \frac{1}{\text{time}} \int m \cdot \frac{dv}{dt}\ dt$$

We are dropping the "total" descriptor on the time variable. The dt terms cancel, so we get

$$F_{avg} = \frac{1}{\text{time}} \int m\ dv$$

Since the mass of the particle is constant, it can be removed from the integral, which is easily evaluated to get

$$F_{\text{avg}} = \frac{1}{\text{time}} \cdot m \cdot \Delta v_{\text{avg}} \tag{19.4}$$

where Δv_{avg} is the average change in the velocity of the gas particle. If there are N gas particles in the container, then the total average force would be

$$F_{\text{avg,total}} = N \cdot \frac{1}{\text{time}} \cdot m \cdot \Delta v_{\text{avg}} \tag{19.5}$$

where Δv_{avg} represents the average change in velocity of the N particles. (Again, we have not constrained the particles to have any particular velocity yet.) This equation is a potential problem, because velocity is a vector in three-dimensional space and so is the change in velocity, Δv_{avg}. However, the three-dimensional velocity can be separated into its one-dimensional components, and the average force separated into three components that are equivalent to each other. Thus, we can consider a one-dimensional problem, then apply our conclusions to the other two dimensions. Let us assume that we are considering the x dimension, corresponding to the dotted line in Figure 19.1. The total force in the x dimension that is applied to the wall is

$$F_{\text{avg,total,x}} = N \cdot \frac{1}{\text{time}} \cdot m \cdot \Delta v_{\text{avg},x}$$

But if we resolve the initial and final velocities of the gas particle in Figure 19.1, we can see that $v_{\text{i}} = -v_{\text{f}}$ (that is, they have the same magnitude but opposite directions). Therefore, in terms of the initial velocity, $\Delta v_{\text{avg},x} = v_{\text{avg},x} - (-v_{\text{avg},x}) = 2v_{\text{avg},x}$ (where we are adding the x subscript to the initial velocity also). The equation for the total average force in the x dimension becomes

$$F_{\text{avg,total},x} = 2 \cdot N \cdot \frac{1}{\text{time}} \cdot m \cdot v_{\text{avg},x} \tag{19.6}$$

Finally, consider a box having dimensions $a \times b \times c$ in the x, y, and z dimensions, as shown in Figure 19.2. What is the time amount in equation 19.6? When the particle is not colliding with the wall, no force is being exerted on it, nor by it on anything else (that's one of the postulates). The time can be as long as it takes for the particle to start at one wall, travel in the x dimension to collide with the other wall, then travel all the way back to the opposite wall. This means that the particle travels twice the x dimension, or a distance of $2a$. From the definition of velocity we have

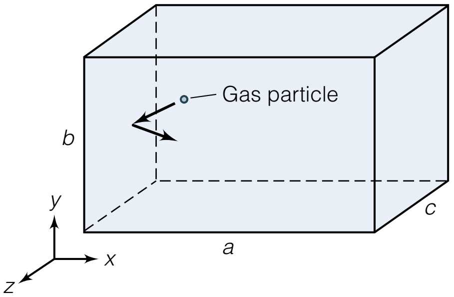


Figure 19.2 A gas particle has a three-dimensional velocity, so an understanding of pressure must consider three dimensions. However, if we assume that all three dimensions are equivalent, the mathematical derivation of pressure is much easier.

$$v_{\text{avg},x} = \frac{2a}{\text{time}}$$

or, rewriting,

$$\text{time} = \frac{2a}{v_{\text{avg},x}}$$

If we substitute this expression for time in the denominator of equation 19.6, we get

$$F_{\text{avg,total},x} = 2N \cdot \frac{1}{\dfrac{2a}{v_{\text{avg},x}}} \cdot m \cdot v_{\text{avg},x}$$

$$F_{\text{avg,total},x} = N \cdot \frac{1}{a} \cdot m \cdot v_{\text{avg},x}^2 = \frac{N \cdot m \cdot v_{\text{avg},x}^2}{a} \tag{19.7}$$

We recognize that pressure is defined as force per unit area. If we are moving in the x dimension, then the wall we are colliding with has dimensions $b \times c$. (Verify this by looking at Figure 19.2.) The pressure exerted in the x dimension, p_x, is therefore

$$p_x \equiv \frac{\text{force}}{\text{area}} = \frac{F_{\text{avg,total},x}}{b \times c} = \frac{N \cdot m \cdot v^2_{\text{avg},x}}{a \times b \times c}$$

Finally, we note two things. First, in the denominator of the above equation, $a \times b \times c$ is the volume of the container, so we will substitute V for the volume in the denominator. Next, we extend the velocity to three dimensions. Using a Pythagorean-theorem approach to velocity in three dimensions, we can show that

$$v^2_{\text{avg}} = v^2_{\text{avg},x} + v^2_{\text{avg},y} + v^2_{\text{avg},z}$$

where v^2_{avg} is the square of the overall, three-dimensional average velocity. Furthermore, since there is no reason to favor one dimension over the other, the components of the average velocity must be equal to each other. Thus

$$v^2_{\text{avg}} = 3v^2_{\text{avg},x}$$

Using these two ideas, the expression for pressure becomes

$$p = \frac{N \cdot m \cdot v^2_{\text{avg}}}{3V} \tag{19.8}$$

This is the basic expression in kinetic theory for the pressure of an ideal gas. In equation 19.8, pressure has standard SI units of kg/(m·s^2), or N/m^2 (which is consistent with the original definition of pressure as a force per unit area). We define the unit *pascal* (abbreviation Pa) as 1 N/m^2. The pascal is the basic SI unit of pressure, although the *bar* (100,000 Pa) and *atmosphere* (1.01325 bar) are commonly used.

Example 19.1

For 1 mole of He gas, a volume of 25.00 L of gas exerts a pressure of 0.8770 bar. What is the average velocity of the helium atoms in the system?

Solution

We can substitute the various values directly into the expression in equation 19.8, recognizing that the product of the variables $N \cdot m$ is the *molar* mass of He, or 0.004003 kg (in standard units), and that 25.00 L is 25.00(0.001/1) = 0.02500 m^3 (again, in standard units):

$$87{,}700\ \frac{\text{N}}{\text{m}^2} = \frac{(0.004003\ \text{kg})(v^2_{\text{avg}})}{3(0.02500\ \text{m}^3)}$$

Since 1 N = 1 kg·m/s^2, we have

$$87{,}700\ \frac{\text{kg}}{\text{m}\cdot\text{s}^2} = \frac{(0.00400\ \text{kg})(v^2_{\text{avg}})}{3(0.02500\ \text{m}^3)}$$

The various units cancel to give us

$$1.643 \times 10^6\ \frac{\text{m}^2}{\text{s}^2} = v^2_{\text{avg}}$$

Solving, we find that

$$v_{\text{avg}} = 1282\ \frac{\text{m}}{\text{s}}$$

or more than 1 km per second. This is a substantial velocity in terms of personal experience, but not for atoms in the gas phase. Notice that we have converted all units to standard units so that they would cancel.

There is also a simple relationship between the pressure of a monatomic gas and its kinetic energy, which can be considered solely as energy of translation. (We are ignoring electronic and nuclear energies, as we did in our original discussion of partition functions of monatomic gases.) Since the classical expression for kinetic energy is

$$\text{kinetic energy} = \tfrac{1}{2}mv^2$$

we can suggest the following analogous equation for the *average* kinetic energy of the gas particles:

$$E_{\text{avg}} = \tfrac{1}{2}m \cdot v_{\text{avg}}^2 \tag{19.9}$$

Substituting for mv_{avg}^2 in equation 19.8, we find that

$$p = \frac{2NE_{\text{avg}}}{3V}$$

Rewriting this by bringing the volume variable over to the other side, we have

$$pV = \tfrac{2}{3}NE_{\text{avg}} \tag{19.10}$$

This is beginning to look like part of the ideal gas law. In fact, if we relate equation 19.10 to the ideal gas law, which says that $pV = nRT$, we find that

$$NE_{\text{avg}} = \tfrac{3}{2}nRT$$

Finally, if we are considering 1 mole of an ideal gas, N is Avogadro's number and NE_{avg} is a molar energy, $\overline{E}$. The variable n in the above equation is 1 mole, so we have for an ideal gas

$$\overline{E} = \tfrac{3}{2}RT \tag{19.11}$$

where we have defined $N_{\text{A}} \cdot E_{\text{avg}}$ as $\overline{E}$, the molar energy of the gas. In Chapter 17, when we considered the translational energy of a monatomic gas, we found that

$$E = \tfrac{3}{2}NkT$$

For 1 mole of gas, $N = N_{\text{A}}$. Equating the two equations for energy, we find that

$$R = N_{\text{A}}k \tag{19.12}$$

which shows the relationship between Boltzmann's constant and the ideal gas law constant.

19.3 Definitions and Distributions of Velocities of Gas Particles

In the previous section, we were able to relate the average velocity of a sample of ideal gas to the pressure of that gas. So far, we have not defined what we mean by "average velocity."

Actually, there are several ways to define this quantity. First of all, the kinetic theory of gases does not make any presumption about the velocity of any particular gas particle; it could be anything. This does not imply that all possible velocities will exist in any gas sample at equal proportions! For example, the velocities of gas particles *could* be anywhere between zero and the speed of light. The naive presumption would be that the average velocity is $(0 + c)/2 = \frac{1}{2}c$ (where c represents the speed of light in a vacuum). This is clearly not the case, as illustrated by the answer in Example 19.1 above.

In the following discussion, we sometimes use the terms "speed" and "velocity" interchangeably. This is because in such cases we are interested more in the magnitude of the quantity, not the direction. However, in cases where direction is important to the discussion, it is pointed out explicitly.

There are several ways of defining an "average" speed, and there are also ways of determining the distribution of speeds of gas particles in any sample. First, let us consider the use of average speed from the previous section. We have two expressions for the kinetic energy of a gas; they are

$$\overline{E} = \tfrac{3}{2}RT \quad \text{and} \quad N_A E_{\text{avg}} = N_A \cdot \tfrac{1}{2}m \cdot v_{\text{avg}}^2$$

(The second equation comes from multiplying equation 19.9 by Avogadro's number.) Equating the two expressions for the molar energy of the gas,

$$\tfrac{3}{2}RT = N_A \cdot \tfrac{1}{2}mv_{\text{avg}}^2 = \tfrac{1}{2}(N_A \cdot m) \cdot v_{\text{avg}}^2$$

Since $(N_A \cdot m)$ is the molar mass of the gas, we will use M to define the molar mass and rewrite the above equation as

$$\tfrac{3}{2}RT = \tfrac{1}{2}M \cdot v_{\text{avg}}^2$$

We can algebraically rearrange this to solve for v_{avg}. Because we are going to be taking the square root of the square of the average (or "mean") speed, we define this average speed as the *root-mean-square speed,* or v_{rms}. We get

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \tag{19.13}$$

This is one way to define an average speed.

Example 19.2

What is the temperature of the He sample in Example 19.1 if the answer is considered to be v_{rms}?

Solution

The velocity in Example 19.1 was 1282 m/s. Using standard units for all quantities, we have

$$1282\,\frac{\text{m}}{\text{s}} = \sqrt{\frac{3 \cdot \left(8.314\,\frac{\text{J}}{\text{mol·K}}\right) \cdot T}{0.00400\,\frac{\text{kg}}{\text{mol}}}}$$

Notice that we have expressed the mass of the gas in kilogram units. This is necessary for the units to work out properly. We need to decompose the unit J into kg·m^2/s^2; when we do this, the expression above becomes

$$1282\,\frac{\text{m}}{\text{s}} = \sqrt{6235.5 \cdot T\,\frac{\text{m}^2}{\text{s}^2\text{·K}}}$$

$$1.6435 \times 10^6\,\frac{\text{m}^2}{\text{s}^2} = 6235.5 \cdot T\,\frac{\text{m}^2}{\text{s}^2\text{·K}}$$

Canceling all the units but kelvins and solving for T:

$$T = 264 \text{ K}$$

The appropriate units for each variable should be used so that everything cancels properly, leaving kelvins as the only remaining unit.

A root-mean-square speed for gas particles is easy to define but should not obscure a key point: gas particles do not all move at the same speed. Also, as implied at the beginning of this section, not all possible speeds are equally probable. Rather, there is a particular distribution of different gas speeds in any sample. What is the mathematical expression that gives us the distribution of gas speeds?

We start by pointing out that if each dimension is independent, then we can consider distribution functions for each dimension separately. In the x, y, and z dimensions, we can define distribution functions (which are also probability functions) $g_x(v_x)$, $g_y(v_y)$, and $g_z(v_z)$, in which each function focuses on only one of three dimensions. In terms of these functions, the probability of any gas particle having a particular three-dimensional velocity is the product of the one-dimensional probabilities. That is,

$$\text{probability} = g_x(v_x)\,dv_x \cdot g_y(v_y)\,dv_y \cdot g_z(v_z)\,dv_z \tag{19.14}$$

If these probability functions are in fact functions of velocities, then the possible range is $-\infty \rightarrow +\infty$, since we must consider direction as well as magnitude. We will require that each individual probability function sum up to 100% over the entire range of the variable. For the x dimension, this is written mathematically as

$$\int_{v_x=-\infty}^{\infty} g_x(v_x)\,dv_x = 1 \tag{19.15}$$

and similar expressions can be written for g_y and g_z.

A common way to determine the form of the functions represented by equation 19.15 is to understand that if the three dimensions can be considered equivalent, then the overall *three-dimensional probability* is a function of the overall three-dimensional velocity. If we use the symbol $\Gamma(v)$ to indicate the three-dimensional probability function, then this statement implies that

$$g_x(v_x) \cdot g_y(v_y) \cdot g_z(v_z) = \Gamma(v) \tag{19.16}$$

In the left side of equation 19.16, the three one-dimensional probability functions are multiplied together to get the overall three-dimensional probability, but the right side implies that this product must be some function of the *three-dimensional velocity* v. Furthermore, we know a relationship between the overall velocity and its components:

$$v^2 = v_x^2 + v_y^2 + v_z^2 \tag{19.17}$$

We focus on a single dimension, the x dimension, and determine the function $g_x(v_x)$. If we were to take the derivative of equation 19.16 with respect to v_x, we would still have an equality. The problem is that the left side and the right side of equation 19.16 are written in terms of different variables. However, calculus has something called the chain rule, and equation 19.17 gives us a relationship between v and v_x, the two variables of interest here. Taking the derivative of each side of equation 19.16 with respect to v_x:

$$\frac{\partial[g_x(v_x)]}{\partial v_x}\cdot g_y(v_y)\cdot g_z(v_z)=\frac{\partial[\Gamma(v)]}{\partial v_x}$$

$$\frac{\partial[g_x(v_x)]}{\partial v_x}\cdot g_y(v_y)\cdot g_z(v_z)=\frac{\partial[\Gamma(v)]}{\partial v}\cdot\frac{\partial v}{\partial v_x} \tag{19.18}$$

The right side of the second equation shows the influence of the chain rule. The left side of the equations above show that the derivative applies only to the g_x function, since it is the only one of the three functions that depends on v_x.

It turns out that we can determine an expression for $\partial v/\partial v_x$ using equation 19.17 and determining the total derivative of v:

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

$$d(v^2) = d(v_x^2 + v_y^2 + v_z^2)$$

$$2v\,dv = 2v_x\,dv_x + 2v_y\,dv_y + 2v_z\,dv_z$$

In terms of partial derivatives, since all other variables are kept constant, we have $dv_y = dv_z = 0$; therefore,

$$2v\,dv = 2v_x\,dv_x$$

$$\frac{\partial v}{\partial v_x}=\frac{v_x}{v} \tag{19.19}$$

This is the desired result. Substituting into equation 19.18, we have

$$\frac{\partial[g_x(v_x)]}{\partial v_x}\cdot g_y(v_y)\cdot g_z(v_z)=\frac{\partial[\Gamma(v)]}{\partial v}\cdot\frac{v_x}{v}$$

Using standard calculus notation, we will use a prime to indicate a derivative with respect to a variable. The above equation becomes, more succinctly,

$$g_x'(v_x)\cdot g_y(v_y)\cdot g_z(v_z)=\Gamma'(v)\cdot\frac{v_x}{v}$$

If we divide the above equation by $g_x(v_x)\cdot g_y(v_y)\cdot g_z(v_z)=\Gamma(v)$, we can cancel terms on the left and rearrange the variables to get

$$\frac{1}{v_x}\cdot\frac{g_x'(v_x)}{g_x(v_x)}=\frac{1}{v}\cdot\frac{\Gamma'(v)}{\Gamma(v)} \tag{19.20}$$

If we did the same analysis for g_y or g_z, we would get a similar expression, only with different subscripts on the left side.

Equation 19.20 is interesting. All of the terms in v_x are on one side of the equation, and all of the terms in v are on the other side of the equation. If one side of the equation is independent of one variable and the other side of the equation is independent of the other variable, then neither side depends on either variable; that is, the expression on each side equals a constant. Using K to represent this constant, we have

$$\frac{1}{v_x}\cdot\frac{g_x'(v_x)}{g_x(v_x)}=\frac{1}{v}\cdot\frac{\Gamma'(\mathrm{v})}{\Gamma(v)}=K \tag{19.21}$$

Understand that this does not mean that v and v_x do not vary, just that the particular combination of the functions on each side of equation 19.20 does not vary. Understand also that if we performed this analysis for the other two dimensions, we would get the same conclusions for y and z, and so we also have two other relationships with the same constant K:

$$\frac{1}{v_y} \cdot \frac{g_y'(v_y)}{g_y(v_y)} = K \quad \text{and} \quad \frac{1}{v_z} \cdot \frac{g_z'(v_z)}{g_z(v_z)} = K \tag{19.22}$$

Solving any one expression therefore gives us an understanding of all four (including Γ). Let us confine ourselves to the x dimension. We want to know what functions satisfy the expression

$$\frac{1}{v_x} \cdot \frac{g_x'(v_x)}{g_x(v_x)} = K$$

where K is some constant. To simplify the understanding of the derivation, let us rewrite g_x' explicitly as the derivative with respect to v_x:

$$\frac{1}{v_x} \cdot \frac{\dfrac{\partial g_x(v_x)}{\partial v_x}}{g_x(v_x)} = K$$

We can rearrange this expression by collecting all terms in g_x, including the differential, on one side and all terms in v_x itself, including *its* differential, on another side. We get, leaving the variable labels off the function g_x:

$$\frac{dg_x}{g_x} = Kv_x \cdot dv_x$$

We integrate both sides of this equation, remembering to include an integration constant (because we are not integrating between specific limits). The integral on the left side is simply $\ln g_x$, the natural logarithm of the function g_x. The integral on the right side is a simple power function. Because we are trying to isolate a form for g_x, we will put the integration constant on the right side of the equation with the v_x terms. We get

$$\ln g_x = \tfrac{1}{2}Kv_x^2 + C$$

where C is some arbitrary integration constant (whose value will be determined later). Taking the inverse logarithm of both sides, we have a preliminary form for g_x:

$$g_x = e^{(1/2)Kv_x^2 + C} = e^{(1/2)Kv_x^2} \cdot e^C \tag{19.23}$$

That is, the distribution function g_x is an exponential function involving the square of the velocity. Since e^C is just some constant, we can define e^C as the constant A and write equation 19.23 as

$$g_x = Ae^{(1/2)Kv_x^2} \tag{19.24}$$

All that remains are two issues. First, we point out that the above derivation is also applicable to the y and z dimensions, so we can also say that

$$g_y = Ae^{(1/2)Kv_y^2}$$

$$g_z = Ae^{(1/2)Kv_z^2}$$

The constants A and K are the same for all three equations, since we are assuming that each dimension is equivalent. Second, we need to determine what A and K are. It turns out that they are related. For starters, remember that equation 19.15 requires that

$$\int_{v_x=-\infty}^{\infty} g_x(v_x)\, dv_x = 1$$

Using the form of g_x in equation 19.24, this means that

$$\int_{v_x=-\infty}^{\infty} Ae^{(1/2)Kv_x^2}\,dv_x = 1$$

We can use the table of integrals in Appendix 1 to show that

$$A = \left(\frac{-K}{2\pi}\right)^{1/2} \tag{19.25}$$

A complete understanding of g_x—and by extension, the entire three-dimensional probability function—depends on determining the constant K.

To determine K, we first use the idea that the velocity in each dimension is equivalent, that is, the average squared velocity in the x dimension is equal to the average squared velocity in the y dimension, which is equal to the average squared velocity in the z dimension:

$$v^2_{\text{avg},x} = v^2_{\text{avg},y} = v^2_{\text{avg},z}$$

(We used this idea in the derivation of equation 19.8.) Since the average kinetic energy of a single gas particle is

$$E_{\text{avg}} = \tfrac{1}{2}m \cdot v^2_{\text{avg}}$$

we can use the definition of the average squared velocity to get

$$E_{\text{avg}} = \tfrac{1}{2}m(v^2_{\text{avg},x} + v^2_{\text{avg},y} + v^2_{\text{avg},z})$$

or, by using the equivalence of the velocity components:

$$E_{\text{avg}} = \tfrac{3}{2}m \cdot v^2_{\text{avg},x}$$

where we are arbitrarily using the x component of the average squared velocity. Comparing this with equation 19.11:

$$E_{\text{avg}} = \frac{3}{2}m \cdot v^2_{\text{avg},x} = \frac{1}{N} \cdot \frac{3}{2}RT$$

If N were Avogadro's number of particles, the above equation would give us

$$\tfrac{3}{2}m \cdot v^2_{\text{avg},x} = \tfrac{3}{2}kT$$

(where we have taken advantage of the relationship between R and k). Rearranging, we get

$$v^2_{\text{avg},x} = \frac{kT}{m} \tag{19.26}$$

which we can use to determine the constant K.

In finding K, we use an idea that we developed in statistical thermodynamics about how to calculate an average value for a variable. Recall the definition of an average value as defined in equation 17.3:

$$\overline{u} = \frac{\displaystyle\sum_{j=1}^{\substack{\text{possible}\\\text{values}}} u_j \cdot P_j}{\displaystyle\sum_j P_j} \tag{19.27}$$

where u_j is the particular value of the variable u, P_j is the probability that this particular value shows up in a group of values, and $\overline{u}$ represents the average value of the variable u. (See the problem worked out near the end of section

17.2 for an example of how to use this formula.) For a well-behaved probability function, the summation of all probabilities, $\sum_j P_j$ in the denominator, equals 1, so equation 19.27 becomes

$$\bar{u} = \sum_{j=1}^{\substack{\text{possible}\\ \text{values}}} u_j \cdot P_j$$

Finally, for a function that can have many possible values which are expressed by a smoothly varying probability function, the above summation can be replaced with an integral, so we have

$$\bar{u} = \int_{\text{min}}^{\text{max}} u_j \cdot P_j \, du \tag{19.28}$$

Equation 19.28 was derived using the same conditions describing the distribution of gas velocities. Therefore, we can use equation 19.28 to set up an integral for the average squared velocity in the x dimension. The variable is v_x^2, and the probability function P_j is given by equation 19.24 with the subsequent determination of the pre-exponential constant A. Substituting into equation 19.28, we have for the average squared velocity:

$$v_{\text{avg},x}^2 = \int_{-\infty}^{+\infty} v_x^2 \cdot \left(\frac{-K}{2\pi}\right)^{1/2} \cdot e^{(1/2)Kv_x^2} \, dv_x \tag{19.29}$$

Since equation 19.29 is an even function of the variable v_x, we can divide the range in half, from 0 to $+\infty$ rather than $-\infty$ to $+\infty$, and multiply the value of that integral by 2. Therefore,

$$v_{\text{avg},x}^2 = 2\left(\frac{-K}{2\pi}\right)^{1/2} \int_0^{+\infty} v_x^2 \cdot e^{(1/2)Kv_x^2} \, dv_x \tag{19.30}$$

where all constants have been removed to outside the integral. The integral in equation 19.30 has a known form; from Appendix 1, we use $\int_0^\infty x^2 e^{-bx^2/2}\,dx$ (where in equation 19.30, $x = v_x$) equals $\pi^{1/2}/[2^{1/2}(-K)^{3/2}]$. Substituting into equation 19.30:

$$v_{\text{avg},x}^2 = 2\left(\frac{-K}{2\pi}\right)^{1/2} \frac{\pi^{1/2}}{2^{1/2}(-K)^{3/2}} \quad \text{which must equal } \frac{kT}{m}$$

where the last part is taken from equation 19.26. Most of the terms on the K side cancel. Solving:

$$\frac{1}{-K} = \frac{kT}{m}$$

$$K = -\frac{m}{kT} \tag{19.31}$$

We therefore have for the distribution function g_x:

$$g_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} \tag{19.32}$$

Similar one-dimensional distribution functions are easily written for g_y and g_z.

Equation 19.32, and the two parallel functions for the y and z dimensions, do not directly give the *three*-dimensional probability function. We have defined the product of the three unidimensional probabilities as Γ:

$$\Gamma(v) = g_x(v_x) \cdot g_y(v_y) \cdot g_z(v_z)$$

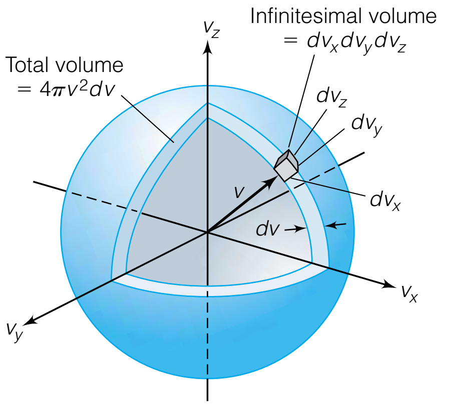


Figure 19.3 In three dimensions, any infinitesimal change in velocity is represented by a spherical shell about the origin. Therefore, the infinitesimal for integrating $G(v)$ from 0 to ∞ must take the spherical symmetry into account.

This is the probability function for the velocities of gas molecules in three dimensions.

If we want to focus on the *scalar* part of the velocities of the gas species, we do not include the fact that velocity as a vector can be positive or negative. We will get a slightly different probability distribution function. This function, labeled $G(v)$, also has a normalization requirement:

$$\int_0^\infty G(v)\, dv = 1$$

In this case, the integration limits are 0 to ∞, rather than $-\infty$ to $+\infty$. Also, because the magnitude of any velocity vector is independent of its direction, each value in $G(v)$ actually represents a spherical shell of possible velocity vectors, as demonstrated in Figure 19.3. There is thus a $4\pi v^2$ component as part of the infinitesimal. (This is akin to the argument used to get a physically useful description for the $1s$ wavefunction for the hydrogen atom.) Using the linear probability functions g_x, g_y, and g_z, we get

$$G(v)\, dv = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_y^2/2kT}\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_z^2/2kT} \cdot 4\pi v^2\, dv$$

This equation simplifies by collecting the exponential terms and writing them as an exponential of the square of the overall velocity, and also by collecting the $(m/2\pi kT)^{1/2}$ terms. We get

$$G(v)\, dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \cdot e^{-mv^2/2kT}\, dv \tag{19.33}$$

This three-dimensional probability distribution function of the velocity magnitudes is called the *Maxwell-Boltzmann distribution.* It can be plotted versus velocity (much like the Planck distribution of light intensity can be plotted versus wavelength). This distribution depends on the mass of the gas particle and the (absolute) temperature. Figure 19.4 shows various plots for different gases at different temperatures. This expression is a special case of the Maxwell-Boltzmann distribution mentioned in statistical thermodynamics, where the E in the exponential refers to the kinetic energies of the particles moving in three dimensions.

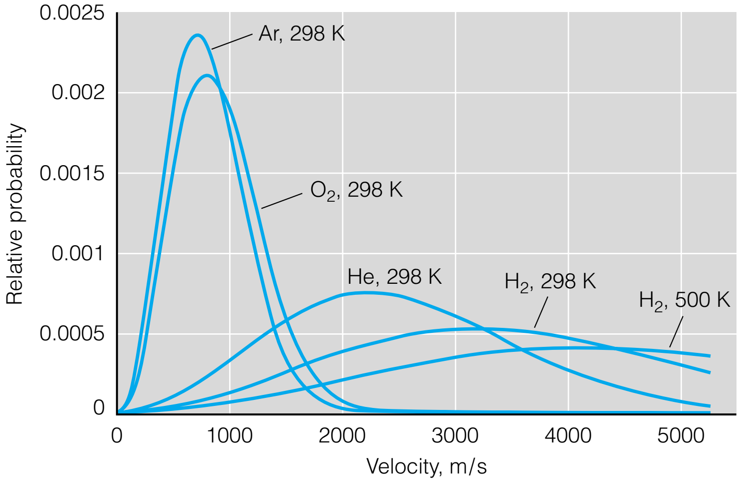


Figure 19.4 Distributions of speeds for various gases. Note how the curve for H_2 is shifted to higher velocities at 500 K. These curves are collectively called Maxwell-Boltzmann distributions.

Now that the probability distribution function has been found, different "average" speeds can be defined. For example, each plot in Figure 19.4 peaks at some maximum, implying that there is some speed that has the highest population among the gas particles at any particular temperature. We can find an expression for this *most probable speed* by taking the derivative of equation 19.33 with respect to v, setting the derivative to zero (because the slope at a maximum is equal to zero), and solving for the velocity at this maximum point. We get

$$v_{\text{most prob}} = \left(\frac{2kT}{m}\right)^{1/2} \tag{19.34}$$

where m is the mass of a single gas particle. In molar quantities, this equation is

$$v_{\text{most prob}} = \left(\frac{2RT}{M}\right)^{1/2} = \sqrt{\frac{2RT}{M}} \tag{19.35}$$

where M is the molar mass of the gas particles.

Example 19.3

What is the most probable speed of He atoms if the gas temperature is 264 K? (Notice that this is the temperature calculated from Example 19.2.)

Solution

Using the molar mass of He (in kg units) and equation 19.35:

$$v_{\text{most prob}} = \left[\frac{2\left(8.314\,\frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(264\text{ K})}{0.00400\,\frac{\text{kg}}{\text{mol}}}\right]^{1/2}$$

After decomposing the J unit into its base units, we have

$$v_{\text{most prob}} = \left(1{,}097{,}448\,\frac{\text{m}^2}{\text{s}^2}\right)^{1/2}$$

$$v_{\text{most prob}} = 1048\text{ m/s} = 1.048 \times 10^3\text{ m/s}$$

The most probable speed is always a little lower than the root-mean-square speed, as a comparison between equations 19.13 and 19.35 shows. Both definitions of average speeds have only the mass of the particle and the absolute temperature of the gas as variables. The other terms are constants.

Finally, now that we have a distribution function $G(v)$ for the velocities, we can determine another average speed. Again, we will use equation 19.28, from statistics, to determine another average value for the speed. Using the idea that

$$\overline{u} = \int_{\text{min}}^{\text{max}} u_j \cdot P_j\, du$$

we will use $G(v)$ as our probability function P_j and v, the velocity, for the variable u_j. The *average* (or *mean*) *speed*, $\overline{v}$, is found by solving the expression

$$\overline{v} = \int_{v=0}^{\infty} v\left[4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \cdot v^2 \cdot e^{-mv^2/2kT}\right] dv$$

Again, this integral can be evaluated using the integral table in Appendix 1. We find that

$$\overline{v} = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \sqrt{\frac{8RT}{\pi M}} \tag{19.36}$$

where again m is the mass of a single gas particle and M is the molar mass of the gas sample. This definition of an average speed also varies only with the mass of the particle and the absolute temperature of the gas.

Example 19.4

Consider a sample of Ar gas. Determine the temperature of the gas if the following velocities were equal to 500.0 m/s:

a. v_{rms}
b. $v_{\text{most prob}}$
c. $\overline{v}$
d. Do the relative temperatures meet expectations?

Solution

We will need to solve for temperature using each of the expressions for the average velocity.

a. For v_{rms}, we have

$$500.0\ \frac{\text{m}}{\text{s}} = \sqrt{\frac{3\left(8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\cdot T}{0.03995\ \frac{\text{kg}}{\text{mol}}}}$$

$$T = 400.4\ \text{K}$$

b. For $v_{\text{most prob}}$, we have

$$500.0\ \frac{\text{m}}{\text{s}} = \sqrt{\frac{2\left(8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\cdot T}{0.03995\ \frac{\text{kg}}{\text{mol}}}}$$

$$T = 600.6\ \text{K}$$

c. For $\overline{v}$, we have

$$500.0\ \frac{\text{m}}{\text{s}} = \sqrt{\frac{8\left(8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\cdot T}{\pi\left(0.03995\ \frac{\text{kg}}{\text{mol}}\right)}}$$

$$T = 471.7\ \text{K}$$

d. These results show that the most probable speed requires the highest temperature, and the average and root-mean-square speeds require lower temperatures to have the same value for the "average."

Figure 19.5 shows a plot of the probability distribution function of Ar gas at the same temperature, 500 K. On the plot, the v_{rms}, $v_{\text{most prob}}$, and $\overline{v}$ values are marked. The relative ordering of average speeds is similar for all gases, and illustrates the slightly different definitions for each of these quantities. What

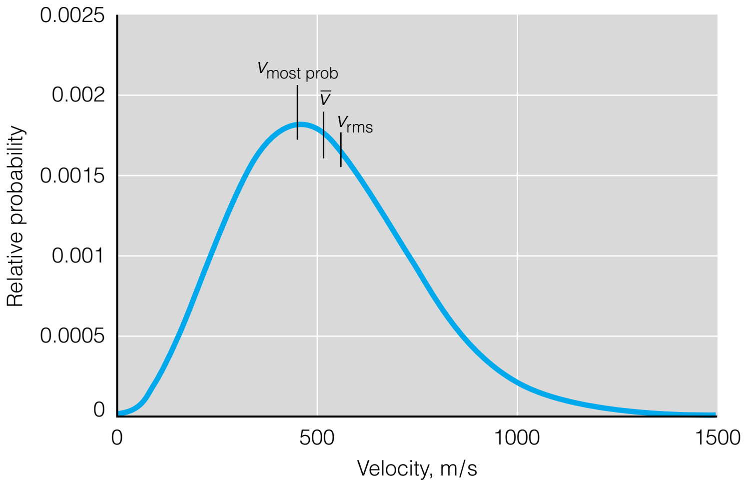


Figure 19.5 In the Maxwell-Boltzmann distribution for argon gas at 500 K, the marks show v_{rms}, $v_{\text{most prob}}$, and $\bar{v}$, showing how they are numerically different.

this plot should point out is that there is no single useful definition of an "average speed" of gas particles, and care should be taken to specify exactly which one is used in any situation.

19.4 Collisions of Gas Particles

One of the statements that define the kinetic theory of gases is that the gas particles are constantly colliding with each other, and during the course of these collisions, the overall energy is conserved. The kinetic theory of gases allows us to understand some of the characteristics of these collisions. In order to understand these characteristics, we need to define some parameters of the gas particles themselves.

For a pure gas, we will assume a *hard-sphere model.* In this model, each gas particle is treated as a spherical particle having a specific radius within which no other gas particle can penetrate. (The best analogy might be to think of gas particles as croquet or billiard balls.) This is illustrated in Figure 19.6. Each gas particle has a radius labeled r, and because each particle is rigid, the nearest that the centers of two particles can approach is twice the radius, or the diameter d. (This is labeled in Figure 19.6.) Because the particles are hard spheres, the presumption is that no two particles can ever get their two centers closer than $2r = d$ to each other. One way of writing this is by defining a potential energy V between any two gas particles:

$V = 0$ if distance between centers is greater than $2r$ (that is, no interaction occurs)

$V = \infty$ if distance between centers is less than $2r$ (not physically possible)

In terms of interparticle collisions, we would like to be able to know three things: the number of collisions any one particle experiences in a given time, the average distance between such collisions, and the net rate of travel of any gas particle through space. The first and second quantities are useful to people studying gas-phase chemical reactions (occurring, for example, in the atmosphere or in space or at high temperatures), and the last quantity is useful for understanding the concepts of diffusion and effusion of gas particles.

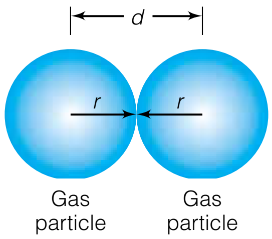


Figure 19.6 In the hard-sphere model of gas particles, each particle is defined as having an impenetrable radius r. Two times r, or the diameter d, is a parameter that will be used in understanding the behavior of gas particles.

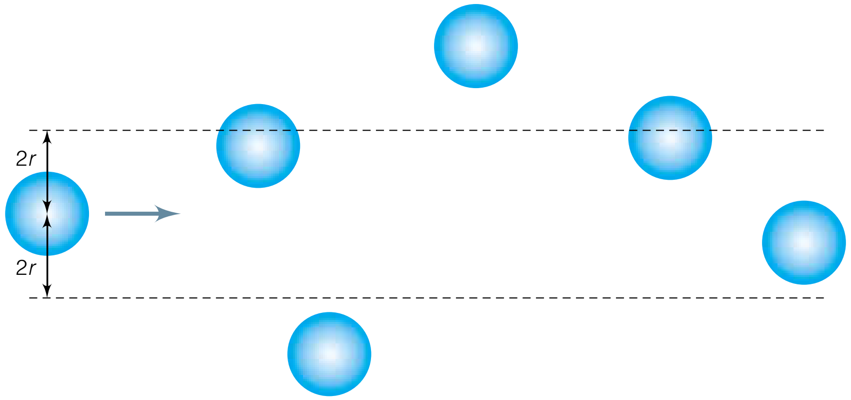


Figure 19.7 In two dimensions, a gas particle P sweeps out an area, colliding with any other gas particle whose center is within $2r$ ($2r = d$) of the center of particle P. In this figure, P will collide with three other gas particles, but two additional gas particles will remain untouched by P. In a real gas, a cross-sectional area of πd^2 is swept out as particle P travels through space.

Suppose we consider a sample of a pure gas. (We will consider gas mixtures later, briefly.) How often does any one gas particle collide with other gas particles, and how far does the particle travel between collisions? We can answer these questions by considering the hypothetical situation of one gas particle moving while all other particles are stationary. As the moving particle P travels through space, it will collide with any gas particle whose *center* gets within $2r$ (twice the radius) of the center of particle P. This is illustrated two-dimensionally in Figure 19.7. In three dimensions, the path of particle P sweeps out a cylinder of space, and any other particle whose center is in that space will collide with particle P. The radius of that cylinder, which is equal to twice the radius ($2r$) or the diameter (d) of the particle, is called the *collision diameter* of the particle. In three dimensions, the cross section of this cylinder is a circle whose area is πd^2; this area is called the *collision cross section* of the gas particle.

Exact distances between colliding particles may be long or short (on the atomic scale), but let us assume that there is some average distance a particle travels between collisions. We call this average the *mean free path* (because it is the average—or mean—distance that the particle is "free" and not colliding with any other particle) and give it the symbol λ. The average volume of the cylinder that is swept out by particle P between collisions is equal to the area of the cylinder (the collision cross section) times its length (the mean free path):

$$\text{average volume between collisions} = \lambda \cdot \pi d^2 \tag{19.37}$$

But if we have N total number of atoms in some given volume V, then the average volume per particle is V/N. Over any macroscopic time scale, these average volumes must be equal:

$$\frac{V}{N} = \lambda \cdot \pi d^2$$

This lets us solve for the mean free path between collisions as

$$\lambda = \frac{V}{\pi N d^2} \tag{19.38}$$

This equation actually provides an estimate for the mean free path, since equation 19.37 considers a cylindrical volume swept out by travel in one dimension, whereas the average volume V/N is more of a three-dimensional average volume. However, equation 19.38 gives us an idea of how far any one gas particle will travel on average before colliding with another gas particle. If we use the ideal gas law to substitute for volume ($V = NkT/p$) in equation 19.38, we get

$$\lambda = \frac{kT}{\pi d^2 p} \tag{19.39}$$

This expression for λ shows how the mean free path varies with other observable values of a gas. At higher temperatures (with everything else in equation 19.39 remaining constant), λ increases. This is consistent with our understanding that if the temperature increases at constant p, the volume of the gas must increase, meaning that there will be more room between individual gas particles. If the pressure increases (with everything else in equation 19.39 remaining constant), λ must decrease. Again, this is consistent, since an increase in pressure will force the gas particles closer together (that is, the volume will decrease) and individual gas particles will collide more frequently and over a shorter distance.

Example 19.5

Assume that the hard-sphere radius of a krypton atom is 1.85 Å. Estimate the mean free path of krypton atoms at 20.0°C and 1.00 bar pressure.

Solution

Recall that 1 Å equals 10^{-10} m. Since the diameter is twice the radius, we will use $d = 3.70 \text{ Å} = 3.70 \times 10^{-10}$ m. Setting up the variables in equation 19.39, we have

$$\lambda = \frac{kT}{\pi d^2 p} = \frac{(1.381 \times 10^{-23}\ \text{J/K})(293.15\ \text{K})}{\pi(3.70 \times 10^{-10}\ \text{m})^2(1.00\ \text{bar})}$$

The units don't automatically work out; instead, we must remember that 100 J = 1 L·bar, and that a liter is defined as $(0.1\ \text{m})^3$. Adding these conversion factors:

$$\lambda = \frac{(1.381 \times 10^{-23}\ \text{J/K})(293.15\ \text{K})}{\pi(3.7 \times 10^{-10}\ \text{m})^2(1.00\ \text{bar})} \times \frac{1\ \text{L}\cdot\text{bar}}{100\ \text{J}} \times \frac{(0.1\ \text{m})^3}{1\ \text{L}}$$

Now the units work out properly, and we calculate λ as

$$\lambda = 9.41 \times 10^{-8}\ \text{m} = 941\ \text{Å}$$

In this case, an average krypton atom travels nearly 300 times its diameter before it collides with another atom. This would be equivalent to a pool ball traveling the length of about 10 pool tables before it struck another ball (on average).

Mean free paths are estimates: they are derived using average values, and they assume that a gas particle is a hard sphere, although many gas molecules aren't even spherical. But mean free paths do provide useful quantitative values for understanding how gas particles interact.

Example 19.6

Assume that a nitrogen molecule acts as a hard sphere with radius 1.60 Å. If you have a vacuum chamber that is 1.00 m on a side, what pressure would it have to be pumped down to in order that a nitrogen molecule has a reasonable chance of not colliding with another nitrogen molecule going from one side to the other (that is, the mean free path is 1.00 m)? Assume a temperature of 22.0°C.

Solution

If the radius of the molecule is 1.60 Å, then the diameter d is 3.20 Å. The question is essentially asking what pressure is necessary for a mean free path of 1.00 m. Using equation 19.39:

$$1.00 \text{ m} = \frac{(1.381 \times 10^{-23} \text{ J/K})(295.15 \text{ K})}{\pi(3.20 \times 10^{-10} \text{ m})^2 \cdot p}$$

Again, in order for the units to work out properly, several conversion factors must be applied (see Example 19.5):

$$1.00 \text{ m} = \frac{(1.381 \times 10^{-23} \text{ J/K})(295.15 \text{ K})}{\pi(3.20 \times 10^{-10} \text{ m})^2 \cdot p} \times \frac{1 \text{ L}\cdot\text{bar}}{100 \text{ J}} \times \frac{(0.1 \text{ m})^3}{1 \text{ L}}$$

$$1.00 = \frac{(1.381 \times 10^{-23})(295.15)}{3.14159(3.20 \times 10^{-10})^2 \cdot p} \times \frac{1 \text{ bar}}{100} \times \frac{(0.1)^3}{1}$$

Solving for p:

$$p = 1.27 \times 10^{-7} \text{ bar}$$

This pressure, about one ten-millionth of an atmosphere, is easily obtainable in the laboratory (using oil diffusion pumps, for example).

Now that we know roughly how far a gas particle typically travels between collisions, we can determine an *average collision frequency,* which tells us about how many times a gas particle comes in contact with another gas particle each second. Collision frequency is a useful concept to apply to gas-phase chemical reactions. We will start with a simple estimate from classical mechanics. Using the definition

$$\text{average speed} = \frac{\text{distance}}{\text{time}}$$

we can use the mean free path as our distance and one of the definitions of average speed defined earlier in this chapter. A frequency is usually defined as the reciprocal of time. In this case, "frequency" is interpreted as the number of collisions per second, so it will have units of s^{-1}. Using the average speed $\bar{v}$, we apply the definition of average velocity from equation 19.36 and the mean free path from equation 19.38 to get an *average collision frequency* z:

$$z = \frac{\bar{v}}{\lambda} = \frac{\left(\dfrac{8kT}{\pi m}\right)^{1/2}}{\dfrac{V}{\pi N d^2}} = \frac{\pi N d^2 \sqrt{8kT}}{V\sqrt{\pi m}} \tag{19.40}$$

If we recognize that the fraction N/V is the density ρ of gas (in units of number of gas particles per m^3, or $1/\text{m}^3$), then we can substitute for V and N in equation 19.40 to get

$$z = \frac{\pi \rho d^2 \sqrt{8kT}}{\sqrt{\pi m}}$$

This expression can be made more accurate by recognizing that a collision of two masses m involves the motion of two particles *with respect to each other.* As with any such motion, we should consider the reduced mass μ of the particles involved, not the absolute mass m. For any two equivalent masses m, the reduced mass is $m/2$. (Show this.) Therefore, substituting $m/2$ for m in the above expression, we get a more realistic equation for the average collision frequency:

$$z = \frac{\pi \rho d^2 \sqrt{16kT}}{\sqrt{\pi m}} \tag{19.41}$$

The *total* number of collisions per second per unit volume, symbolized by Z, is related to z times the density of the gas. However, simply multiplying z and ρ counts all collisions for all particles. This overcounts the total collisions by 2, since each collision represents a collision of two particles. Including a factor of $\frac{1}{2}$ to make up for this overcounting, we have for Z:

$$Z = \frac{1}{2} \cdot z \cdot \rho = \frac{2\pi \rho^2 d^2 \cdot \sqrt{kT}}{\sqrt{\pi m}} \tag{19.42}$$

The 2 from the $\frac{1}{2}$ term cancels with $\sqrt{16}$ in the numerator to leave $\sqrt{4}$, which equals 2. Because the density unit here is $1/\text{m}^3$, the units on Z are $1/\text{s}\cdot\text{m}^3$.

Example 19.7

Xenon has a very large hard-sphere diameter of 4.00 Å. For a 1-mole sample of Xe gas with a volume of 0.02271 m^3, at conditions of 1.000 bar and 273.15 K, determine the following:

a. The average collision rate
b. The total collision rate per cubic meter
c. The total collision rate

Solution

This example asks for z, Z, and Z times the total volume (to get a collision rate for all of the gas particles in the sample). The density ρ is $(6.02 \times 10^{23}$ molecules$)/(0.02271\ \text{m}^3) = 2.65 \times 10^{25}\ \text{m}^{-3}$ and the mass of a xenon atom is $(0.1313\ \text{kg})/(6.02 \times 10^{23}) = 2.181 \times 10^{-25}$ kg.

a. We get

$$z = \frac{\pi(2.65 \times 10^{25}\ \text{m}^{-3})(4.00 \times 10^{-10}\ \text{m})^2\sqrt{16(1.381 \times 10^{-23}\ \text{J/K})(273.15\ \text{K})}}{\sqrt{\pi \cdot 2.181 \times 10^{-25}\ \text{kg}}}$$

Consider the units in the radicals in both the numerator and denominator: they reduce to $\sqrt{\text{J}}/\sqrt{\text{kg}}$, and upon decomposing the unit J into more fundamental units, become $\sqrt{\text{kg}\cdot\text{m}^2/\text{s}^2}/\sqrt{\text{kg}} = \sqrt{\text{m}^2/\text{s}^2} = \text{m/s}$. All of the meter units in the numerator cancel, leaving s^{-1} as the only remaining unit (as it should be for a frequency).

$$z = 3.95 \times 10^9\ \text{s}^{-1}$$

or almost 4 billion collisions per second.

b. The total collision rate per unit volume is therefore

$$Z = \tfrac{1}{2} \cdot z \cdot \rho = \tfrac{1}{2}(3.95 \times 10^9\ \text{s}^{-1})(2.65 \times 10^{25}\ \text{m}^{-3})$$

$$Z = 5.23 \times 10^{34}\ \text{m}^{-3}\cdot\text{s}^{-1}$$

which says that in every cubic meter of sample, 5.23×10^{34} collisions occur per second.

c. However, our volume is only 0.02271 m^3. The total number of collisions occurring in 1.000 mol of Xe is therefore

$$5.23 \times 10^{34}\ m^{-3}\cdot s^{-1} \cdot 0.02271\ m^3 = 1.19 \times 10^{33}\ s^{-1}$$

This total number of collisions is roughly equal to N_A gas particles (that is, 1 mole) having four billion collisions per second. (Verify this by multiplying those two quantities together—and don't forget the factor of 2!)

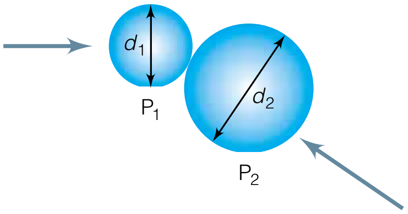


Figure 19.8 If the gas particles involved in the collision are of different types, then two different masses and diameters enter into the equation for collision frequencies.

If two different gases are present in a sample, then the number of collisions of any particular gas particle can be divided into collisions with like particles and collisions with different particles. We can therefore define a mean free path between collisions of unlike particles as well as a collision rate between unlike particles. For two particles P_1 and P_2 that have diameters d_1 and d_2 (see Figure 19.8) and masses m_1 and m_2, we give (but do not derive) the mean free path for a P_1 particle hitting a P_2 particle, labeled $\lambda_{1\rightarrow 2}$:

$$\lambda_{1\rightarrow 2} = \sqrt{\frac{m_2}{m_1 + m_2}}\,\frac{V}{\pi\left(\frac{d_1 + d_2}{2}\right)^2 N_2} \tag{19.43}$$

where N_2 is the number of particles of gas P_2. Since N_2/V is the density of P_2 gas particles, we can rewrite this expression in terms of the density ρ_2:

$$\lambda_{1\rightarrow 2} = \sqrt{\frac{m_2}{m_1 + m_2}}\,\frac{1}{\pi\left(\frac{d_1 + d_2}{2}\right)^2 \rho_2} \tag{19.44}$$

Similarly, we can define a collision rate for a P_1 particle hitting a P_2 particle, labeled $z_{1\rightarrow 2}$:

$$z_{1\rightarrow 2} = \frac{\pi\rho_2\left(\frac{d_1 + d_2}{2}\right)^2\sqrt{8kT}}{\sqrt{\pi\mu_{12}}} \tag{19.45}$$

where μ_{12} is the reduced mass of the two particles:

$$\mu_{12} = \frac{m_1 \cdot m_2}{m_1 + m_2} \tag{19.46}$$

(Because m_1 and m_2 are different, we cannot use $m/2$ here as we did for equation 19.41.) Mean free paths and collision rates for P_2 hitting P_1 are found by simply exchanging the subscripts 1 and 2 where they appear in equations 19.43–19.45. The total number of collisions per second per unit volume can be determined from equation 19.45 and its counterpart:

$$Z_{1\rightarrow 2} = \frac{\pi\rho_1\rho_2\left(\frac{d_1 + d_2}{2}\right)^2\sqrt{8kT}}{\sqrt{\pi\mu_{12}}} \tag{19.47}$$

Use of these expressions is left for the end-of-chapter exercises.

19.5 Effusion and Diffusion

An understanding of how gas particles travel within the gas sample itself helps us understand the effusion and diffusion of gases. *Effusion* is the passage of gas particles through a barrier (like a small hole) into a different region where no

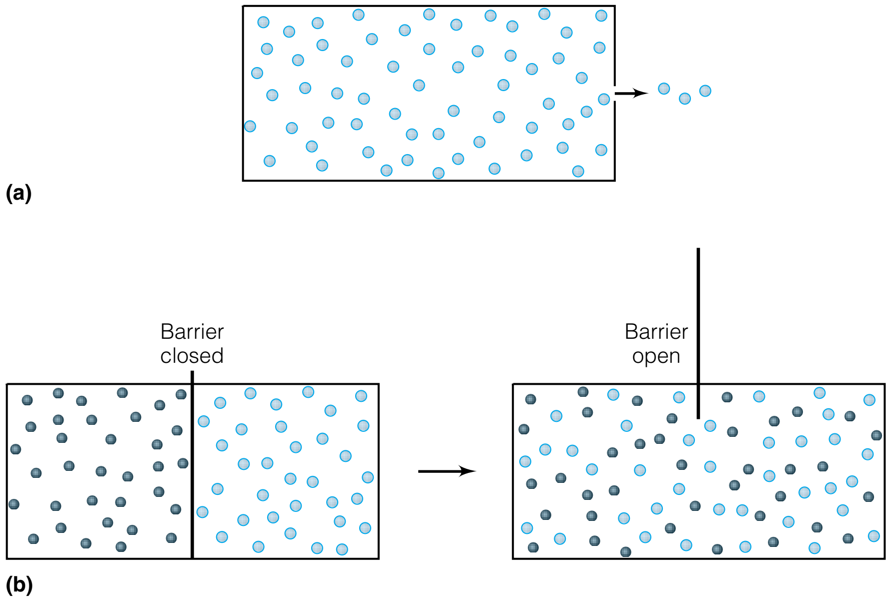


Figure 19.9 (a) Effusion is the movement of gas particles from a system into the surroundings, usually through a small hole or holes. Typically, the surroundings are deficient in gas particles, and effusion is usually so slow that the pressure of the gas inside the system can be considered constant. (b) Diffusion is the movement of gas particles within a system and is caused by concentration differences. For example, two gases may be separated by a partition, but after that partition is lifted the two gases will diffuse and ultimately will become thoroughly mixed.

particles (and usually no gas of any sort) existed previously. It is usually a slow process, so that the concentration of gas particles in the original system is approximately constant. *Diffusion* is the passage of gas particles (or solute species, if in solution) from one part of a system to another due to unequal concentrations of that gas within the system, with the total pressure constant in the system (that is, the transport isn't due to pressure gradients). Figure 19.9 illustrates the difference.

Effusion can be understood if we consider the velocity of the gas particles in one dimension. We start by pointing out that the effusion rate must be proportional to the average velocity in that dimension, since we expect that the faster the gas particles are traveling, the faster they can escape out of a hole in the system. This idea can be written mathematically as

$$\text{rate of effusion} \propto v_{\text{avg}}$$

We have already determined a probability density function that describes the distribution of velocities among the gas particles. It was, for the x dimension,

$$g_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}$$

If we want to know the number of gas particles that are passing through some small hole with area A per second (represented as dN/dt), then we need to determine the number of gas particles that are approaching the hole *from one direction*. This restriction implies that for a chamber filled with gas particles, these particles are slowly leaking out of the chamber but not back into the chamber. (See Figure 19.9a.) If we arbitrarily assign the direction toward the hole in the chamber as the positive direction, the average velocity of the particles approaching the hole is

$$\text{average velocity} = \int_{v_x=0}^{\infty} v_x \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} \cdot dv_x \qquad \textbf{(19.48)}$$

This integral has a known form and can be simplified.* We get

$$\text{average velocity} = \left(\frac{kT}{2\pi m}\right)^{1/2} \tag{19.49}$$

Thus we have

$$\text{rate of effusion} = \frac{dN}{dt} \propto \left(\frac{kT}{2\pi m}\right)^{1/2}$$

The only other factors involved are the number (density) of gas particles in the system, N/V or ρ, and the area A that the gas particles are actually passing through. Both factors are directly related to the effusion rate: as either increases, the effusion rate increases. We can therefore write

$$\frac{dN}{dt} = A\rho\left(\frac{kT}{2\pi m}\right)^{1/2} \tag{19.50}$$

as the rate of effusion of gas particles through an area A. Using the ideal gas law $pV = NkT$, we can substitute for N/V and get

$$\frac{dN}{dt} = A\frac{p}{kT}\left(\frac{kT}{2\pi m}\right)^{1/2}$$

which simplifies to

$$\frac{dN}{dt} = Ap\left(\frac{1}{2\pi mkT}\right)^{1/2} \tag{19.51}$$

Curiously, a part of this expression is very similar to part of the translational partition function of a monatomic gas, and is proportional to the thermal de Broglie wavelength (see Chapter 17).

Example 19.8

Iron metal is confined to a small cell that has a small hole of 0.5 mm diameter. At a temperature of 2050 K, the vapor pressure of the Fe inside the cell is 1.00 mmHg. Estimate the number of atoms of Fe that effuse through the hole per second.

Solution

As with many of these examples, having consistent units is important. The area of the hole is $\pi[(0.5\text{ mm})/2]^2$, or 0.196 mm^2, which is 1.96×10^{-7} m^2. A pressure of 1.00 mmHg should be converted to pascals (1 Pa = 1 N/m^2 = 0.00750 mmHg), making it 133 Pa. Using the mass of a single Fe atom:

$$\frac{dN}{dt} = (1.96 \times 10^{-7}\text{ m}^2)\left(133\ \frac{\text{N}}{\text{m}^2}\right)\left[\frac{1}{2\pi(9.27 \times 10^{-26}\text{ kg})(1.381 \times 10^{-23}\text{J/K})(2050\text{ K})}\right]^{1/2}$$

---

*Specifically, one would perform a substitution and recognize the resulting integral as the form

$$\int_0^\infty x^n e^{-ax^p}\,dx = \frac{\Gamma(k)}{pa^k} \qquad \left(k = \frac{n+1}{p}\right)$$

$\Gamma(k)$ is called a *gamma function* and is a well-known mathematical function. By definition, $\Gamma(1) = 1$. Apply this formula to equation 19.48 and see if you can get equation 19.49. Do not confuse this use of the gamma variable with the three-dimensional probability function!

The units inside the square root term are $s^2/(kg^2 \cdot m^2)$, so the square root of this unit is s/(kg·m). Outside of the square root term, only the unit N (newton) remains. Recalling that $N = kg \cdot m/s^2$, our overall units reduce to 1/s, which is an appropriate unit for a rate. Solving:

$$\frac{dN}{dt} = 2.03 \times 10^{17}\ s^{-1} \qquad \text{or } 2.03 \times 10^{17} \text{ Fe atoms per second}$$

This is equivalent to 0.3 micromoles per second, or about 16.7 micrograms per second. At this rate, it would take over 16 hours for 1 gram of Fe to effuse through the hole.

Because the use of tiny-holed chambers to study the effusion of gases was pioneered by the Dutch scientist Martin Knudsen in the early 1900s, such chambers are called *Knudsen cells* and this type of effusion is termed *Knudsen effusion.* Knudsen cells are still used for vaporizing high-melting materials in vacuum systems; for example, they are used in the semiconductor industry to manufacture computer chips.

Diffusion is the movement of gas particles through another gas due to concentration differences (see Figure 19.9b). It is one example of what is called a *transport property,* which describes the net movement of (in this case) matter or energy through a nonuniform medium. Other transport properties include viscosity, electrical conductivity, thermal conductivity, and sedimentation of particles in fluids.

For our purposes, we will assume that two different gases are present in a system, separated at first. The initial question to consider is similar to that for effusion: assuming motion in a single dimension (arbitrarily the x dimension), at what rate are the gas particles approaching a planar surface of area A that is perpendicular to their direction of travel? The system in question is illustrated in Figure 19.10. Experiments have shown that the rate of flow of gas particles P_1 across a plane of area A and into a region filled by gas particles P_2 is given by the expression

$$\frac{dN_1}{dt} = -D \cdot A \cdot \frac{dc_1}{dx} \tag{19.52}$$

where dN_1/dt is the rate at which gas particles pass through the plane, A is the area of the plane, dc_1/dx is the concentration gradient of gas particles P_1 in the x dimension, and D is a proportionality constant called the *diffusion coefficient.* Equation 19.52 is known as *Fick's first law of diffusion.* (Fick's second law of diffusion involves the change in c_1 over time—rather than over distance—and will not be considered here.) The negative sign in equation 19.52 implies that the direction of flow of increasing amount of P_1 particles is opposite the direction of increasing concentration of P_1 particles: that is, particles tend to flow from high concentrations to low concentrations.

If the concentration c_1 has units of amount per volume, the differential dc_1/dx has units $(amt/m^3)/m$. Since area has SI units of m^2, the diffusion coefficient must have units of m^2/s in order for the diffusion rate dN_1/dt to have units of amount per second. For historical reasons, units for D are typically given as (non-SI) cm^2/s. The specific value of D depends not only on the identity of the gas P_1, but also on the identity of the gas that P_1 is diffusing into. With respect to Figure 19.10, it should be noted that the gas particles P_2 are also diffusing into the left side of the system, but for now we are ignoring this

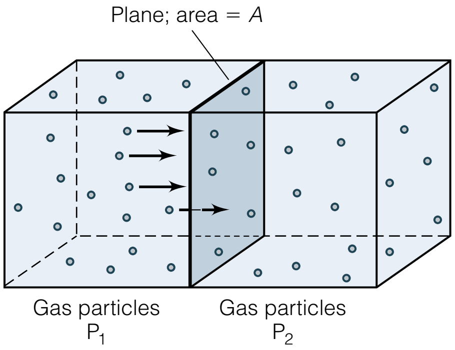


Figure 19.10 Diffusion is understood by determining the rate at which gas particles P_1 move through some area A and into an area occupied by gas particles P_2.

and concentrating on the flow of P_1 into the right side of the system. (The equation we will derive will apply to either gas, ultimately.)

An understanding of diffusion therefore centers on determining the diffusion coefficient D. We can actually define two types of diffusion coefficients. The first one describes the diffusion of a gas particle through itself (the case in which the gases represented by P_1 and P_2 are actually the same chemical species). This is called *self-diffusion.* There is also the case in which two gases have different identities, and they diffuse into each other. This is called *mutual diffusion.*

In either case, we expect that the diffusion coefficient is related to the average velocity of the gas particles as well as its mean free path. This is indeed the case. Without going through the detailed derivation, it can be shown that the self-diffusion coefficient D is

$$D = \frac{3\pi}{16} \cdot \lambda \cdot \bar{v} = \frac{3}{8d^2\rho} \cdot \sqrt{\frac{RT}{\pi M}} \qquad \textbf{(19.53)}$$

where all variables have been previously defined. Experimental measurements of diffusion coefficients can be used with the equation to estimate the hard-sphere diameter, d, for polyatomic gas molecules. As for accuracy, equation 19.53 results compare fairly well with experimental diffusion coefficients, when using hard-sphere diameters determined from other methods.

For mutual diffusion coefficients, the derivation is even more complicated because there are three mean free paths to consider, between like gas particles (there are two like-particle mean free paths, one for each gas) and between different gas particles. The final answer is

$$D_{12} = \frac{3}{8} \cdot \sqrt{\frac{RT}{2\pi\mu}} \cdot \frac{1}{(r_1 + r_2)^2\rho_{\text{tot}}} \qquad \textbf{(19.54)}$$

where μ is the reduced (molar) masses of the two gases, r_1 and r_2 are the hard-sphere radii of P_1 and P_2, and ρ_{tot} is the total particle density of the gases. Equation 19.54 shows the curious fact, observed experimentally, that the diffusion coefficient does not depend on the mole fractions of each gas in the system, as one might expect.

Many diffusion coefficients for gases are on the order of 10^{-1} cm^2/s. Diffusion coefficients can also be defined for liquid and solid phases. Although the kinetic theory of gases does not apply directly to these phases, there are some conceptual similarities. However, diffusion coefficients for condensed phases are much lower than for gases, especially for solids at normal temperatures. Diffusion coefficients for solids are typically in the range of 10^{-19} to 10^{-25} cm^2/s.

From the concept of a mean free path, it should be understood that as gas particles diffuse, they do not travel in a straight line into a new region. Rather, as they collide with other gas particles, their direction changes continuously but—as the concentration gradient requires—they ultimately end up moving in the direction of lower concentration. Such a path is called a *random walk* and is illustrated (in two dimensions) in Figure 19.11. In reality, random walks of individual gas particles are three-dimensional, but the overall result is the same: a net displacement from one part of the system (of high concentration) to another part of the system (of low concentration). How long does it take any one particle to move a certain distance, given this random-walk description of its motion? That is, can we determine the net displacement of a gas particle?

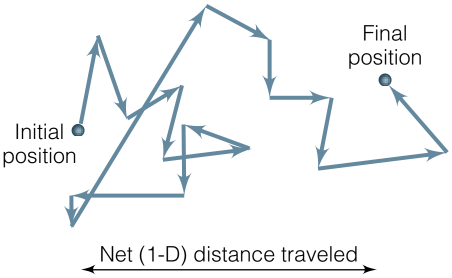


Figure 19.11 Over time, a gas particle travels some net distance. However, in doing so the particle doesn't take a direct path. Rather, its actual travel is a complicated "dance" in three-dimensional space. The true path of any one gas particle is called a random walk.

The answers to these questions are the topic of one of Einstein's seminal manuscripts that were published in 1905. (Other topics include a rationalization of the photoelectric effect in terms of Planck's theory of light, and special relativity). In trying to understand the phenomenon called Brownian motion, Einstein applied kinetic theory and determined an expression for the average displacement of a particle due to interparticle collisions and mean free paths. In considering the one-dimensional net displacement of gas particles from their starting point, we need to recognize that they can travel in either a positive or a negative direction, so that the average one-dimensional displacement, Δx_{avg}, is simply zero. To get around that, we will consider the average of the *square* of the displacement, $(\Delta x)^2_{\text{avg}}$, since by squaring the displacement we make all values positive.

For the average of the square of the one-dimensional displacement, Einstein derived the expression

$$(\Delta x)^2_{\text{avg}} = 2 \cdot D \cdot t \qquad \textbf{(19.55)}$$

where D is the diffusion coefficient from Fick's law of diffusion and t is the time. This one-dimensional diffusion equation is called the *Einstein-Smoluchowski equation.* (Marian Smoluchowski was a Polish physicist who also considered the theoretical basis of Brownian motion.) The units on $(\Delta x)^2_{\text{avg}}$ are m^2 (if meters are the units used in D), so by taking the square root of $(\Delta x)^2_{\text{avg}}$ we get a root-mean-square average distance that a gas particle travels from an initial point over some time t. Since the total distance is the sum of the displacements in the x, the y, and the z dimensions, it should be easy to generalize equation 19.55 to all dimensions, add them, and get an average three-dimensional displacement as

$$(\text{3-D displacement})^2_{\text{avg}} = 6 \cdot D \cdot t \qquad \textbf{(19.56)}$$

Under controlled conditions where there is no convection, gas particle displacements are not as large as one might think, as the following example shows.

Example 19.9

The diffusion coefficient D_{12} of NH_3 in air is about 0.219 cm^2/s at normal atmospheric pressures and room temperature. A container of ammonia is opened at the front of a lecture hall. Assuming that the air is perfectly still and that diffusion alone accounts for the transport of NH_3 in the air, how long before ammonia molecules can be expected to diffuse 20.0 m away from the source?

Solution

In this example, we are solving for the time t that it takes for gaseous ammonia molecules to travel 20.0 meters in three dimensions. Using equation 19.56:

$$(20.0\ \text{m})^2 = 6\left(0.219\ \frac{\text{cm}^2}{\text{s}}\right) \cdot t\left(\frac{1\ \text{m}}{100\ \text{cm}}\right)^2$$

The last term in the expression above is needed to convert cm to m. Solving for time:

$$t = 3.04 \times 10^6\ \text{s}$$

It would take over a month for NH_3 molecules to diffuse 20.0 meters! This example illustrates the importance of convection, rather than diffusion, in the transport of gas molecules under real conditions.

Contrary to expectations, gas diffusion is rather slow. For example, in one minute the average displacement of NH_3 molecules under the above conditions is only about 9 cm. The *total distance* that the ammonia gas molecule travels in its random walk among the other gas particles, however, is over 36 km! (This can be estimated by calculating an average speed of NH_3 and multiplying by the total time, which is 60 seconds.) That is, only 0.0002% of the distance traveled has gone into actually moving away from the original starting point. Although this may seem strange, it is consistent with our understanding of gas behavior on the basis of the kinetic theory.

Finally, note that both equation 19.51, defining effusion, and equations 19.53 and 19.54, which relate to diffusion, are inversely proportional to the square root of the mass of the gas particle (or the reduced mass of the two-component system). This idea, expressed as

$$\text{rate of gas effusion or diffusion} \propto \frac{1}{\sqrt{\text{mass}}} \tag{19.57}$$

is called *Graham's law.* Scottish scientist Thomas Graham discovered this relationship in 1831, almost 30 years before the development of the kinetic theory. (Among other things, Graham also studied and defined colloids and proposed the idea of "denaturing" alcohol so it would not be ingested.) Graham's law is a good generality but is often overused, in part because conduction and convection in fluids can so easily and effectively overwhelm pure effusion and diffusion—as Example 19.9 demonstrates. Also, most "examples" of Graham's law (like the classic HCl/NH_3 vapors-in-a-tube demonstration) use only the masses of the individual gases themselves. This would be accurate if the experiment were demonstrating *ef*fusion. However, as equation 19.54 shows, the reduced mass μ must be used in cases where *dif*fusion through another gas is considered.

19.6 Summary

One of the goals of physical chemistry is to develop models that explain the behavior of chemical phenomena. Since quantum mechanics is a crucial model in chemistry, it is ironic that the physical behavior of gases can be understood by using only classical mechanics. By assuming that gas particles are constantly moving, and by treating them as hard spheres, we can apply classical concepts and calculate how fast they are moving (on average) through space and how fast they move through other gases. As part of that understanding, we are able to determine how often gas particles collide with each other, roughly how far they travel before they collide, and how quickly they propagate from a system (effusion) or within a system (diffusion). Although this chapter has focused on the behavior of gases, we can recognize that some of these ideas are also applicable to condensed phases. Indeed, the behavior of liquids and solids can be partially understood by applying classical mechanics, also. Such applications can be found in more advanced texts. The point of this chapter is that the physical behavior of gases is one of the better-understood phenomena in chemistry.

EXERCISES FOR CHAPTER 19

19.2 Postulates and Pressure

19.1. Define "postulate" in the scientific sense. You may have to consult a good dictionary that can define scientific terms appropriately. Why don't we try to prove the postulates of the kinetic theory of gases?

19.2. What is the kinetic energy of a single atom of mercury that has a speed of 200 m/s? (This is a good speed for Hg atoms at room temperature.) What is the kinetic energy of a mole of Hg atoms having that speed?

19.3. Show geometrically that the following vector relationship $v^2 = v_x^2 + v_y^2 + v_z^2$ is correct and, by analogy, $v_{\text{avg}}^2 = v_{\text{avg},x}^2 + v_{\text{avg},y}^2 + v_{\text{avg},z}^2$.

19.4. At a temperature of 273.15 K and pressure of 1 atm or 1.01325 bar, many gases have an approximate volume of 22.4 L. (This is a very useful approximation.) What are the average speeds of **(a)** He atoms and **(b)** Kr atoms under these conditions? Compare your answer for part a with the answer in Example 19.1.

19.5. Use equation 19.8 and the classical definition of kinetic energy to argue that the average kinetic energy of a gas is the same for all gases at the same absolute temperature.

19.6. Interstellar space can be considered as having 10 molecules of hydrogen per cubic centimeter and an average temperature (far away from stars!) of 2.7 K. Determine **(a)** the pressure of hydrogen in interstellar space and **(b)** the average speed of the hydrogen molecules. Compare these answers with values under normal Earth conditions.

19.3 Velocities

19.7. Compare the temperatures required to have an rms-average speed of 200, 400, 600, 800, and 1000 m/s for Cs atoms. Note that the average speeds form a pattern. What is the pattern of the calculated temperatures?

19.8. If relativistic effects were ignored, what temperature is required for hydrogen atoms to have an rms-average speed of 3.00×10^8 m/s? What do you think is the potential for actually achieving this temperature?

19.9. Verify equation 19.25. You will need to consult the table of integrals in Appendix 1, and use the idea that $K = -(-K)$.

19.10. Distinguish between the definitions of g, G, and Γ as the three probability functions defined in the derivation of the Maxwell-Boltzmann distribution.

19.11. Show that the constant K, as defined by $1/v_x \cdot g_x'(v_x)/g_x(v_x)$ and $1/v \cdot \Gamma'(v)/\Gamma(v)$, has the same value for $1/v_y \cdot g_y'(v_y)/g_y(v_y)$ and $1/v_z \cdot g_z'(v_z)/g_z(v_z)$.

19.12. Derive equation 19.34.

19.13. What is the ratio of $v_{\text{rms}}/v_{\text{most prob}}$ for any gas at a given temperature?

19.14. Use the Maxwell-Boltzmann distribution function to numerically estimate (that is, do not evaluate the integral) the percentage of O_2 molecules at 300 K moving **(a)** between 10 and 20 m/s; **(b)** between 100 and 110 m/s; **(c)** between 1000 and 1010 m/s; **(d)** between 5000 and 5010 m/s; and **(e)** between 10,000 and 10,010 m/s. Each interval has the same absolute value. What do your answers tell you about the distribution of velocities among the gas molecules?

19.15. Current research that focuses on low temperatures uses crossed laser beams to slow down gas atoms (the phrase "optical molasses" is a good analogy) so much that their "temperature" is close to absolute zero.

(a) If atoms of Rb are moving at 1 cm/s, what is the approximate "temperature" of the Rb gas? (You can use any definition of "average temperature" for this estimate.)

(b) How relevant is the word "temperature" to systems like the one described? Develop arguments for and against the applicability of the term to gas atoms trapped in optical molasses.

19.16. Use the form of $G(v)$ to find $\overline{v^2}$, then take the square root of the answer you get and show that you get the definition of v_{rms}, the root-mean-square speed.

19.17. Compare relative values of v_{rms}, $v_{\text{most prob}}$, and $\bar{v}$. Will they always have the same relative values, or can variations in conditions like temperature or molar mass change their relative magnitudes?

19.4 Collisions

19.18. Vacuum systems use some gauges that measure pressures in millitorr (where 760 torr = 1 atm). Express the answer from exercise 19.6 in units of millitorr.

19.19. Derive equation 19.41.

19.20. Use the conditions of exercise 19.6 to determine the mean free path between hydrogen molecules in interstellar space if $d = 1.10$ Å for hydrogen.

19.21. Explain why the molecular diameter for argon, at 2.6 Å, is about the same as that for molecular hydrogen, at 2.4 Å, even though hydrogen is a much smaller atom than argon.

19.22. Tanks of nitrogen gas are often pressurized to 2400 psi (pounds per square inch) at room temperature. What is the mean free path of a nitrogen molecule, $d = 3.20$ Å, under these conditions? There are 14.7 psi in 1.00 atm.

19.23. For a given sample of gas (which has a certain molar mass, collision diameter, and so on), what variable(s) does the average collision frequency depend on?

19.24. The vapor pressure of Hg at room temperature (taken as 22.0° C) is 0.001426 mmHg. What is the average collision frequency of gaseous Hg atoms in a system that contains only Hg? Use $d = 2.4$ Å, and use the ideal gas law to determine the density of Hg vapors under these conditions.

19.25. A 1.00-mole sample of Xe gas is kept at a temperature of 298 K. What volume must it have in order to have an average collision frequency of 1 per second? Assume that the collision diameter is 4.00 Å.

19.26. What is the total number of collisions per second per unit volume for the gas system described in the previous exercise?

19.27. What is the total number of collisions per second for the gas system described in the previous exercise? (Note how this question is different from the earlier one.)

19.28. Determine **(a)** the mean free paths, **(b)** the average collision frequencies, and **(c)** the total number of collisions between nitrogen and oxygen molecules in air. Assume standard thermodynamic conditions (273 K and 1 atm) and use $d =$ 3.15 and 2.98 Å for nitrogen and oxygen, respectively.

19.29. Consider a gas mixture containing equal concentrations of argon and helium. Without performing any calculations, determine which is higher: the number of collisions between helium and helium, the number of collisions between argon and argon, or the number of collisions between helium and argon?

19.5 Effusion and Diffusion

19.30. In what ways are effusion and diffusion different? In what ways are they similar?

19.31. Estimate the rate at which Hg effuses out a hole of area 0.10 mm^2 at 295 K. The vapor pressure of Hg at this temperature is 0.0014 mmHg.

19.32. Knudsen effusion cells are used to determine vapor pressures of high-temperature materials. For example, a Knudsen cell is filled with tungsten and heated to 4500 K in a vacuum. Measurements show that the cell loses mass—assumed to be W vapor—at the rate of 2.113 grams per hour out of a hole that is 1.00 mm^2 in area. Calculate the vapor pressure of W at 4500 K.

19.33. Knudsen effusion can be used to estimate the amount of gas entering into a vacuum system from an aperture. If argon gas at 300 K and 0.100 torr is introduced into a vacuum system via a tube that had an inner diameter of 0.01625 inches, how many grams per second of argon are entering the vacuum system? (Watch your units on this one!)

19.34. If an atomically clean metal surface is generated in a vacuum system whose pressure is kept at 1.00×10^{-12} torr, how many atoms of oxygen per second are colliding with each square centimeter of the surface? Assume that any residual gas in the system has the same composition as air, and a temperature of 295K.

19.35. Using equation 19.54, determine the units of D_{12}.

19.36. Determine D for **(a)** He and **(b)** Xe at standard pressure and 25.0°C. Use $d = 2.65$ and 4.00 Å, respectively.

19.37. Use Fick's first law to demonstrate why diffusion stops when a solute (that is, minor component) gas is evenly spread in a system of solvent (that is, major component) gas.

19.38. Verify the approximate value for D_{12} in Example 19.9, using hard-sphere radii of 1.6 Å for ammonia and 1.9 Å as an estimate for air molecules.

19.39. Calculate the total distance traveled by an ammonia molecule in 1 minute using the definition of average velocity from classical mechanics and using an average velocity defined by kinetic theory. Assume $T = 295$K.

19.40. Use the D values from exercise 19.36 to determine how far away from its original position an average atom travels in 1 second if it is He or if it is Xe.

19.41. Consider a variation from the conditions in Example 19.9. Assume that the ammonia is diffusing through an atmosphere of **(a)** helium, or **(b)** SF_6. Will diffusion be faster or slower than through air?

19.42. Use Graham's law to determine the ratio of diffusion through air of HCl and NH_3 vapors. First, use only the masses of HCl and NH_3. Then, determine the reduced masses of (HCl + air) and (NH_3 + air) and determine the ratio of diffusion. Compare the ratios to the experimentally determined ratio of about 0.7. Which ratio represents the better model of reality?

19.43. A recent educational paper claimed that rather than using HCl or NH_3 or other vapors to illustrate diffusion, one can use soluble salts dropped on either sides of a petri dish filled with water. As the salts dissolve, their ions "diffuse" and, with the correct selection of salts, form a precipitate when cation and anion diffuse to the same point. The ratio of distances that the ions travel could be related to their masses, much as Graham's law does for gases. Critique this "demonstration" of diffusion.

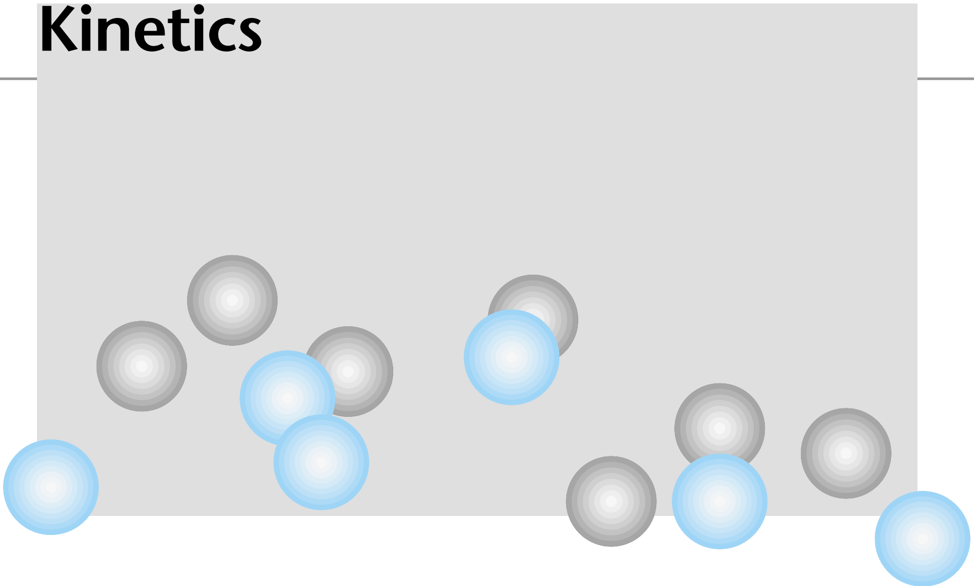
Symbolic Math Exercises

19.44. For 1 mole of He at 298 K, compare graphs of g_x versus v_x and $G(v)$ versus v. What are the similarities and differences in the graphs?

19.45. Use the graph of $G(v)$ from exercise 19.44 to determine what percentage of atoms have a velocity within 1% of **(a)** the root-mean-square speed; **(b)** the most probable speed; and **(c)** the mean speed. Are the percentages similar?

20

Kinetics



ONE MOLECULE OF A REACTANT SPECIES collides with another molecule, chemical bonds are rearranged all at once, and voilà—molecules of product species are formed. This is how it works, right?

Not quite.

Why chemical reactions occur is mainly the focus of thermodynamics. Concepts like energy and entropy are important in understanding whether processes are spontaneous or nonspontaneous. *How* they occur is the main focus of kinetics. A basic understanding of a process includes, foremost, how fast it goes. This is the rate of the reaction. A deeper understanding of a chemical process includes knowing why a particular chemical reaction proceeds as fast or as slow as it does: what are the factors that influence the rate of the reaction? Are the factors controllable, like concentrations or temperatures or available surface area or presence of catalysts? Or are the factors inherent to the process, like the chemical identity of the reactants and products or conditions dictated by thermodynamics? These are all factors that must be considered in order to understand the kinetics of a chemical process.

First and foremost, it needs to be stressed how thermodynamics and kinetics relate to each other. Thermodynamics tries to determine *if*; kinetics tries to determine *how.* Although they occasionally overlap, the two questions *if* and *how* ask two different things. Thermodynamics will tell you if something might occur, but will not tell you (by itself) how long you might have to wait. Kinetics will tell you how fast something might occur, but will not tell you (by itself) if it actually will happen. A proper understanding of any process requires input from both kinetics and thermodynamics.

Kinetics is like classical thermodynamics in that much of it is phenomenological: it is based on observation. Experimental kinetics requires that a person make measurements of a chemical process and then try to explain or generalize it. However, there has been some progress in theoretical kinetics, which we will discuss briefly. In this chapter, we will go over some of the framework that is used to generalize our understanding of chemical kinetics.

20.1 Synopsis

One of the central focuses of kinetics is the determination of rate laws: simple mathematical expressions that tell us how fast a particular chemical reaction will proceed. Rate laws that have similar mathematical forms imply that their reactions behave a certain way as the reaction proceeds in time; we will consider some of those behaviors. Using the tools of calculus, we will be able to derive some simple expressions that will help us predict amounts of reactants and products of reactions that have particular rate laws.

A central part of a rate law for any chemical reaction is its rate constant, which (as its name implies) is a constant for a particular reaction at a particular temperature. This statement implies that the rate law constant does change with temperature, and that's correct. But we also have some simple models for how the rate law constant changes with temperature.

Reactions don't just occur singly; they occur sequentially or in parallel. We will consider how several processes occurring simultaneously affect the amounts of products and reactants. Finally, we recognize that most chemical reactions occur in discrete steps. The overall combination of these steps, called elementary processes, is what makes up the mechanism of a reaction. A proposed mechanism must be consistent with the experimentally determined rate law of a reaction. This requirement puts some restrictions on how we can expect a chemical reaction to occur on an atomic and molecular scale.

Near the end of the chapter, we will consider two interesting types of reactions, branched reactions and oscillating reactions. Not only do such reactions have interesting kinetics, but they have some fascinating applications. Finally, we will discuss a little bit of theoretical kinetics, to leave you with the idea that not all kinetics is phenomenological. More and more, basic physical chemical principles are applied at the molecular level in attempts to describe adequate models for chemical reactions—which are, after all, of fundamental interest to chemists.

20.2 Rates and Rate Laws

One of the most basic descriptions of a chemical reaction is how fast it goes. But when we speak of how fast a reaction goes, we are not thinking "fast" as in a velocity in meters per second. Rather, we are thinking about how quickly amounts (that is, moles) of reactants are converted into amounts (moles) of products. The "quickness" implies that time (in units of seconds, minutes, hours, days, and so on) will be a concern also. The *rate* of a reaction is an indication of how many moles of a reactant or product are reacted or produced over a period of time.

Rates of reactions are a central issue in kinetics. Understand that it is difficult to predict before the fact how fast a reaction will be (although we will explore some of the factors that influence the rate of reactions). A lot of information about kinetics of reactions is experimentally determined. Reaction rates also provide the fundamental information needed to deduce the individual actions that reactant species take in order to make products. (We will consider this near the end of this chapter.)

Furthermore, in a closed system, the rates of most reactions change over time. Typically, amounts of reactants decrease over time. When discussing rates of reactions, it is important to indicate at what point along the extent of the reaction we are. (Extents of reaction, ξ, were discussed previously in Chapter 5.) It is conventional to define rates of reactions as they would be at the very beginning of a chemical process, in which only reactants are present, no products. The rate of a reaction at this extent $\xi = 0$ is called the *rate of initial reaction* or the *initial reaction rate*. In almost all cases, we will be dealing with initial reaction rates.

As defined above, a rate of reaction can be expressed in the change in amount of reactant per some amount of time. Expressed mathematically, this is

$$\text{rate} = \frac{\text{change in amount}}{\text{change in time}} = \frac{\Delta(\text{amount})}{\Delta(\text{time})} \tag{20.1}$$

where the Greek letter capital delta implies "change." If amounts were expressed in moles and time in seconds, a rate would have units of mol/s.

Moles *of what?* This is a necessary distinction, but one that is easy to forget. For example, in the balanced chemical reaction

$$2H_2 + O_2 \longrightarrow 2H_2O \tag{20.2}$$

there are 2 moles of hydrogen reacting with every mole of oxygen to make water. If a rate is expressed as 1.00 mol/s, are we talking about 1 mole of hydrogen gas reacting every second, or 1 mole of oxygen gas? Because of the stoichiometry in equation 20.2, a rate of 1 mole per second is not specific enough to communicate what the actual rate of the reaction is.

However, also because of the stoichiometry of the balanced chemical reaction, rates of reactions in terms of individual reactants and products are related. All one has to do is specify one rate in terms of a single species, and the rate with respect to any other species in the balanced chemical reaction can be determined. For a general chemical reaction

$$aA + bB \longrightarrow cC + dD$$

where A and B are the reactants, C and D are the products, and a, b, c, and d are the coefficients of the balanced reaction, one can express the rate of the reaction in terms of four different changing amounts:

$$\begin{aligned} &\text{rate} = \frac{1}{a}\cdot\left(-\frac{\Delta[\mathrm{A}]}{\Delta\text{time}}\right) = \frac{1}{b}\cdot\left(-\frac{\Delta[\mathrm{B}]}{\Delta\text{time}}\right) \\ \text{or}\quad &\text{rate} = \frac{1}{c}\cdot\left(+\frac{\Delta[\mathrm{C}]}{\Delta\text{time}}\right) = \frac{1}{d}\cdot\left(+\frac{\Delta[\mathrm{D}]}{\Delta\text{time}}\right) \end{aligned} \tag{20.3}$$

The convention is to express rates in terms of reactants as negative, since the concentrations of reactants are decreasing as the reaction progresses. Conversely, rates expressed in terms of products are positive, since product amounts are increasing as the reaction proceeds. To remind ourselves of these facts, we write the − and + signs explicitly in equation 20.3. The brackets [ ] imply amounts, usually moles or molarity (that is, concentration) units. The coefficients a, b, c, or d in the denominators are the scaling factors from the stoichiometry of the balanced chemical equation. These allow a rate to be expressed as the same numerical value no matter which change in amount is used to express the rate.

For infinitesimal changes, instead of expressing changes using Δ, we should use the differential d. The expressions in equation 20.3 become

$$\begin{aligned} &\text{rate} = -\frac{1}{a}\cdot\frac{d[\mathrm{A}]}{dt} = -\frac{1}{b}\cdot\frac{d[\mathrm{B}]}{dt} \\ \text{or}\quad &\text{rate} = +\frac{1}{c}\cdot\frac{d[\mathrm{C}]}{dt} = +\frac{1}{d}\cdot\frac{d[\mathrm{D}]}{dt} \end{aligned} \tag{20.4}$$

where we are using the variable t to represent time. Again, numerically, these different ways to express the rate are the same. They simply refer to the change in amount of different chemical species.

It is common to express the rate of a reaction in terms of the absolute change in the amount of one species, then scale the other rates proportionately. This way, the numerical value of the rate of the reaction differs depending on the species used to express the rate as well as the coefficients in the balanced chemical reaction. One of the expressions in equation 20.4 can be rearranged to get

$$\text{rate} = -\frac{d[\mathrm{A}]}{dt} = -\frac{a}{b} \cdot \frac{d[\mathrm{B}]}{dt} \tag{20.5}$$

However, with this convention, the numerical values of the rates with respect to the different species are no longer the same.

Example 20.1

Referring to equation 20.2, if the reaction proceeds at a rate of −5.00 mol/min with respect to H_2, what are the rates with respect to O_2 and H_2O?

Solution

Using the balanced chemical reaction and equation 20.5, the rate expressed in terms of oxygen will be $\frac{1}{2}(-5.00\ \text{mol/min}) = -2.50\ \text{mol/min}$. The rate expressed in terms of H_2O will be $+\frac{2}{2}(5.00\ \text{mol/min})$ or $+5.00$ mol/min. Notice that we are still, by convention, expressing the rate in terms of reactants as negative and the rate in terms of products as positive. If we wanted to express the rate of this reaction as an invariant value, it would be ±2.50 mol/min. (The sign would depend on whether the intent is to express the disappearance of reactants or the appearance of products.)

Rates of reactions can be expressed numerically and usually refer to the rate at a specific extent of the reaction, typically at the beginning (that is, $\xi = 0$). This numerical rate is accurate only for that point, however. If conditions change—as the reaction progresses or as the amounts of reactants and products change, or even if the same reaction is set up but with different initial conditions—the numerical value of the rate is usually no longer valid. (We will discuss an exception to this shortly.) It would be useful to determine the rate of a reaction in a way that is more applicable to differing conditions, especially changes in initial concentrations of reactants.

For most reactions, the initial rate is related to the initial amounts of some or all of the reactants. Experimentally, what is found is that the initial rate is proportional to the concentration (that is, molarity) of some or all of the reactants raised to some exponent. Expressing this concept mathematically, for some general reaction "$a\mathrm{A} + b\mathrm{B} \rightarrow$ products":

$$\text{rate} \propto [\mathrm{A}]^m \cdot [\mathrm{B}]^n \tag{20.6}$$

In order to make this proportionality an equality, a proportionality constant k is introduced:

$$\text{rate} = k \cdot [\mathrm{A}]^m \cdot [\mathrm{B}]^n \tag{20.7}$$

The proportionality constant k is the *rate constant* for the reaction, and is usually independent of the exact concentrations of A and B (or any other species whose concentration appears in the algebraic expression) but is usually dependent on temperature. The exponents m and n are called *orders*; the way equation 20.7 is written, m is called the *order with respect to A*, and n is the *order with respect to B*, and so on, if other terms exist. Orders are usually small positive whole numbers, but they may be negative whole numbers, zero, or even fractions. The sum of all orders of the algebraic expression is the *overall order* of the reaction.

The complete expression in equation 20.7 is called a *rate law*. Rate laws *must be determined experimentally*. Sometimes they are simple; sometimes they can be very complicated. But in all cases, they must be determined by setting up a chemical reaction under different conditions of initial concentrations, measuring the initial rates by some experimental method, and algebraically deducing the individual orders and the numerical value of the rate constant k. The rate constant k should also have units that will give a proper unit for the overall rate (which is usually mol/s or M/s). Although problems involving rate laws may already be familiar to you, the following example illustrates the mathematical tactic for determining a simple rate law from experimental data.

Example 20.2

For a general reaction "$a\text{A} + b\text{B} \rightarrow$ products," the following initial rates are determined experimentally when reactions are set up with the initial amounts indicated in units of molarity, M.

[A] (M)	[B] (M)	Initial rate (M/s)
1.44	0.35	5.37×10^{-3}
1.44	0.70	2.15×10^{-2}
2.89	0.35	2.69×10^{-3}

Assuming that the rate law can be written as

$$\text{rate} = k \cdot [\text{A}]^m \cdot [\text{B}]^n$$

determine the values of m, n, and k.

Solution

The tactic in determining orders is to set up two rate law expressions using two different sets of numbers, and then divide one expression by the other. Select the sets so that the concentration of one of the species cancels (as will k). Then, the order with respect to the other species can be determined by inspection or by taking the logarithm of the resulting equation.

Using the first and second sets of data, we can substitute into the general form of the rate law to get two equations:

$$5.37 \times 10^{-3}\ \frac{\text{M}}{\text{s}} = k(1.44\ \text{M})^m \cdot (0.35\ \text{M})^n$$

and

$$2.15 \times 10^{-2}\ \frac{\text{M}}{\text{s}} = k(1.44\ \text{M})^m \cdot (0.70\ \text{M})^n$$

Dividing the first equation by the second, we have

$$\frac{5.37 \times 10^{-3}\ \text{M/s}}{2.15 \times 10^{-2}\ \text{M/s}} = \frac{k(1.44\ \text{M})^m \cdot (0.35\ \text{M})^n}{k(1.44\ \text{M})^m \cdot (0.70\ \text{M})^n}$$

The units on the left cancel, as do the k's on the right. Notice that the $(1.44\ \text{M})^m$ also cancels on the right side *no matter what value m is* . We get

$$0.25 = (0.50)^n$$

Since 0.25 is $\frac{1}{4}$ and 0.50 is $\frac{1}{2}$, it is seen by inspection that the exponent n equals 2. (You should verify this.) Using the first and third sets of experimental data, we can construct a similar comparison:

$$\frac{5.37 \times 10^{-3}\ \text{M/s}}{2.69 \times 10^{-3}\ \text{M/s}} = \frac{k(1.44\ \text{M})^m \cdot (0.35\ \text{M})^n}{k(2.89\ \text{M})^m \cdot (0.35\ \text{M})^n}$$

Units and k's cancel to give

$$2 = (0.50)^m$$

Since 0.50 is equal to $\frac{1}{2}$, we can see that $m = -1$. (You should verify this also.) Finally, to determine the value of the rate constant k, we can substitute any set of data into the rate law. It should not matter which data set is used for this. Using the first set:

$$5.37 \times 10^{-3}\ \frac{\text{M}}{\text{s}} = k(1.44\ \text{M})^{-1} \cdot (0.70\ \text{M})^2$$

Solving:

$$5.37 \times 10^{-3}\ \frac{\text{M}}{\text{s}} = k \cdot 0.340\ \text{M}$$

$$k = 1.59 \times 10^{-2}\ \text{s}^{-1}$$

The units on k are appropriate to give a unit of M/s on the rate. Verify that the second and third sets of experimental data give a similar value for k.

Students should be aware that in real cases the numerical treatment does not work out as perfectly as it did in the above example. Some level of mathematical sophistication, and the application of logarithms, may be necessary to determine the orders in the rate law. Example 20.6 shows one such case where use of logarithms is necessary to determine the order of the reaction.

20.3 Characteristics of Specific Initial Rate Laws

There are several simple forms of rate laws, so it is common to discuss them and their particular characteristics. Although many rate laws depend on the amounts of more than one component, we will focus on rate laws of the type

$$\text{rate} = k \cdot [\text{A}]^n \tag{20.8}$$

in this section. What is the behavior of the rate when the order with respect to A has various common whole number values?

To apply calculus to equation 20.8, we need to rewrite the quantity "rate" in terms of a change in amount over some period of time. We do this by using the forms in equation 20.4. If we are focusing on a reactant species A, the rate is

$$\text{rate} = -\frac{d[\text{A}]}{dt} \tag{20.9}$$

where the [A] term can be an amount in moles or in concentration units. We will presume a concentration unit—molarity—at this point. The general equation whose properties we hope to understand is

$$-\frac{d[\text{A}]}{dt} = k \cdot [\text{A}]^n \tag{20.10}$$

A *first-order reaction* is one whose kinetics follow a rate law where the order is 1; that is,

$$-\frac{d[\mathrm{A}]}{dt} = k \cdot [\mathrm{A}]^1 \qquad \textbf{(20.11)}$$

All spontaneous radioactive processes and many chemical processes (including many metabolic processes in the body) are first-order reactions. We can rearrange equation 20.11 to isolate all terms in the species A on one side, and all other variables on the other:

$$\frac{d[\mathrm{A}]}{[\mathrm{A}]} = -k \cdot dt \qquad \textbf{(20.12)}$$

In this equation, we are leaving out the 1 exponent, since it is understood to be present. If we presume that at some initial time t_i, the amount of A is represented as $[\mathrm{A}]_\mathrm{i}$, and at some final time t_f the amount of A is represented as $[\mathrm{A}]_\mathrm{f}$, we can integrate both sides of the above equation between the limits of the respective variable:

$$\int_{[\mathrm{A}]_\mathrm{i}}^{[\mathrm{A}]_\mathrm{f}} \frac{d[\mathrm{A}]}{[\mathrm{A}]} = \int_{t_\mathrm{i}}^{t_\mathrm{f}} -k \cdot dt$$

The integral on the left side is the natural logarithm of A, evaluated between the two limits. The integral on the right side is simply the variable t (time) evaluated between its two limits. After performing the evaluations on either side, we get

$$\ln \frac{[\mathrm{A}]_\mathrm{f}}{[\mathrm{A}]_\mathrm{i}} = -k(t_\mathrm{f} - t_\mathrm{i})$$

The leading negative sign on the right side is usually removed by switching the numerator and denominator in the logarithm term. (This is a mathematical property of logarithms.)

$$-\ln \frac{[\mathrm{A}]_\mathrm{i}}{[\mathrm{A}]_\mathrm{f}} = -k(t_\mathrm{f} - t_\mathrm{i})$$

The minus signs cancel to yield

$$\ln \frac{[\mathrm{A}]_\mathrm{i}}{[\mathrm{A}]_\mathrm{f}} = k(t_\mathrm{f} - t_\mathrm{i}) \qquad \textbf{(20.13)}$$

Typically when measuring a process the initial time is set to 0 and the final time is simply the elapsed time. We will use the symbol $[\mathrm{A}]_0$ to indicate the initial amount of A at time 0 and $[\mathrm{A}]_t$ to stand for the amount of A at some time t. Using these conventions, equation 20.13 is commonly written as

$$\ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = k \cdot t \qquad \textbf{(20.14)}$$

where t represents the elapsed time. This is the basic equation that relates how the concentration of A varies over time for a first-order reaction. Equation 20.14 is known as the *integrated form of a first-order rate law* (or more simply, the *integrated rate law*). Note that $[\mathrm{A}]_0$ and $[\mathrm{A}]_t$ *must* have the same units (and can even be percentages, where $[\mathrm{A}]_0$ is usually considered 100%, that is, whatever the original amount was). Also, k and t must have the same units of time.

Example 20.3

One example of a first-order reaction is the isomerization of hydrogen isocyanide to hydrogen cyanide:

$$\text{HNC (g)} \longrightarrow \text{HCN (g)}$$

If the rate constant at a particular temperature is $4.403 \times 10^{-4}\ \text{s}^{-1}$, what *mass* of HNC remains after 1.50 hr if a 1.000-gram sample of HNC was present at the beginning of the reaction?

Solution

We can use equation 20.14 directly by recognizing that $k = 4.403 \times 10^{-4}$ 1/s, $[A]_0 = 1.000$ g, and $t = 1.50$ hr, which we must convert to units of seconds: $t = 5400$ s. With these numbers, we get

$$\ln \frac{1.000\ \text{g}}{[A]_t} = \left(4.403 \times 10^{-4}\ \frac{1}{\text{s}}\right)(5400\ \text{s})$$

$$\ln \frac{1.000\ \text{g}}{[A]_t} = 2.378$$

Taking the inverse logarithm of both sides, we get

$$\frac{1.000\ \text{g}}{[A]_t} = 238.5$$

Solving for the final amount:

$$[A]_t = 0.00419\ \text{g}$$

Just over 0.4% of the original material remains as the unreacted HNC.

There are two other ways of expressing equation 20.14 mathematically. One way is to take the inverse logarithm of both sides, then rearrange the variables so we get an expression for $[A]_t$ as the time varies. We get

$$[A]_t = [A]_0 \cdot e^{-kt} \tag{20.15}$$

which shows that the amount at any time t follows a negative exponential function of time. (You should note that the initial amount, $[A]_0$, is a constant for a given experiment.) Negative exponential functions have the characteristic of having a maximum value at the variable $t = 0$, and declining monotonically and asymptotically toward zero. Figure 20.1 shows the general trend for $[A]_t$ over time. The speed with which the amount $[A]_t$ approaches zero is dictated by the rate constant k.

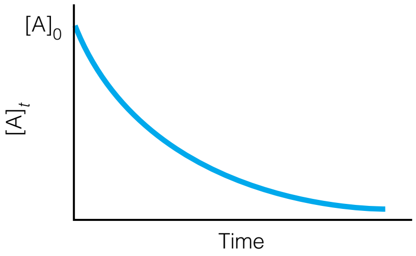


Figure 20.1 For a first-order reaction, the concentration at any time, labeled $[A]_t$, decreases in a characteristic negative exponential way. The rate at which it approaches a zero concentration is dictated by the value of the rate constant. Mathematically, the plot of $[A]_t$ does not reach 0 until $t = \infty$.

Another way to rewrite equation 20.14 is to separate the logarithms of the numerator and denominator in the fractional term. We can do that and rewrite the equation as

$$\ln [A]_t = \ln [A]_0 - kt \tag{20.16}$$

This equation has the form of a straight line $y = mx + b$, where y is $\ln[A]_t$, the slope m is $-k$, x is t (the elapsed time), and the y-intercept $b = \ln[A]_0$. (Again, since $[A]_0$ is a constant, so is the logarithm of $[A]_0$. We usually ignore the units on $[A]_0$ and $[A]_t$—you can take a logarithm only of a pure number, not of a unit—but we require that they be expressed in the same

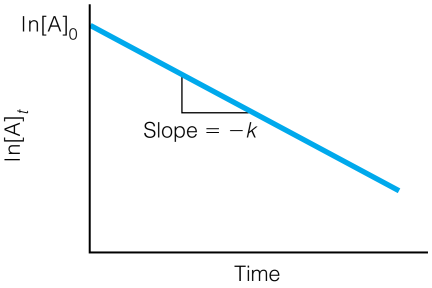


Figure 20.2 For a first-order reaction, a plot of the natural logarithm of $[A]_t$ versus time gives a straight line whose slope is $-k$ and y-intercept is $\ln[A]_0$, the logarithm of the initial amount. This is characteristic of a first-order reaction; no other order reaction gives a straight line when plotting $\ln[A]_t$ versus time.

concentration unit.*) Therefore, a plot of $\ln[A]_t$—the natural logarithm of the amount of A at various times—versus the time will give a straight line, as seen in Figure 20.2. This line will have a slope of $-k$, the negative of the rate constant, with $\ln[A]_0$, the logarithm of the original amount, as the y-intercept. A straight-line plot of $\ln[A]_t$ versus t will be produced only if the reaction is indeed first-order with respect to A.

Finally, there is a very popular concept connected to first-order reactions: half-life. The *half-life* of a first-order reaction is the amount of time necessary for half of the original amount to react. We can use equation 20.14 to derive a simple expression for the half-life, $t_{1/2}$:

$$\ln\frac{100\%}{50\%} = k \cdot t_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k} \tag{20.17}$$

Notice that $t_{1/2}$ is independent of the original amount $[A]_0$! It is related only to the first-order rate constant of the reaction. Because all natural radioactive processes are first-order processes, the concept of half-life is a common one.

Not all reactions are first-order. A *second-order reaction* is defined by the rate law

$$-\frac{d[A]}{dt} = k \cdot [A]^2 \tag{20.18}$$

We can do the same thing for this equation as we did for the first-order rate law: rearrange the variables in A on one side and the variables in time on the other side:

$$-\frac{d[A]}{[A]^2} = k \cdot dt \tag{20.19}$$

Again, integrating both sides of the equation between the final and initial limits, and presuming again that we start at some initial time $t_i = 0$ so that t represents elapsed time, we get for the *integrated second-order rate law*

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = k \cdot t \tag{20.20}$$

As the concentration of the reactant species A changes with time, its concentration fits the above equation (as long as the reaction follows second-order kinetics with respect to the species A). We can rearrange equation 20.20 into a form that mimics a straight-line equation:

$$\frac{1}{[A]_t} = k \cdot t + \frac{1}{[A]_0} \tag{20.21}$$

where now y is $1/[A]_t$, x is time again, the slope m is given by the rate constant k, and the y-intercept b is represented by $1/[A]_0$, the reciprocal of the initial amount of species A. Figure 20.3 shows how a plot of a second-order reaction

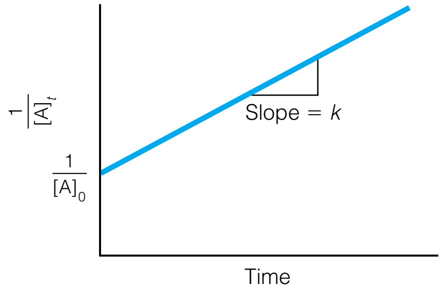


Figure 20.3 For a second-order reaction, a plot of the reciprocal of $[A]_t$, $1/[A]_t$, versus time gives a straight line whose slope is k and y-intercept is $1/[A]_0$, the reciprocal of the initial amount. This is characteristic of a second-order reaction; no other order reaction gives a straight line when plotting $1/[A]_t$ versus time.

---

*Equation 20.16 can be written as

$$\ln\frac{[A]_t}{\text{concn unit}} = \ln\frac{[A]_0}{\text{concn unit}} - kt$$

as a way of addressing the units issue. This chapter is simply avoiding overcomplicating the equations.

should look if $1/[A]_t$ were plotted on the y-axis and time were plotted on the x-axis. Once again, the appearance of a straight line for a plot of $1/[A]_t$ versus t is specific for a second-order reaction. Plotting these variables will yield a straight line if and only if the reaction is second order with respect to the species A.

Example 20.4

What are the units for the rate constant for a second-order reaction that has the rate law

$$-\frac{d[A]}{dt} = k \cdot [A]^2$$

if the units on the amounts are molarity?

Solution

The rate itself has units of M/s. If the term $[A]^2$ contributes units of M^2 (molarity squared), then the rate constant must have units of $1/(M\cdot s)$:

$$M^2 \cdot \frac{1}{M \cdot s} = \frac{M}{s}$$

Although this may seem like a strange unit for a rate constant, it is necessary for the dimensional analysis to give the proper units for the experimentally determined rate of the reaction.

Example 20.5

Consider the following reaction:

$$CS_2\ (g) + 3O_2\ (g) \longrightarrow CO_2\ (g) + 2SO_2\ (g)$$

If the rate law for the reaction can be written as

$$-\frac{d[CS_2]}{dt} = \left(3.07 \times 10^{-4}\ \frac{1}{M\cdot s}\right)[CS_2]^2$$

how long will it take for the concentration of CS_2 to drop to half of the initial concentration for the following initial concentrations?

a. 0.05000 mol/L
b. 0.00500 mol/L
c. Comment on the answers.

Solution

This is another half-life problem, but it is not as straightforward as it is for first-order reactions.

a. We can use equation 20.20 by letting $[A]_0 = 0.05000$ mol/L and $[A]_t = 0.02500$ mol/L, which is half of the original concentration:

$$\frac{1}{0.02500\ \text{mol/L}} - \frac{1}{0.05000\ \text{mol/L}} = \left(3.07 \times 10^{-4}\ \frac{1}{M\cdot s}\right) \cdot t$$

$$40.00\ \frac{L}{mol} - 20.00\ \frac{L}{mol} = \left(3.07 \times 10^{-4}\ \frac{1}{M\cdot s}\right) \cdot t$$

$$20.00\ \frac{L}{mol} = \left(3.07 \times 10^{-4}\ \frac{1}{M\cdot s}\right) \cdot t$$

The units L/mol cancel with the M unit in the denominator of the right side; solving for t:

$$t = 65{,}100 \text{ s}$$

which is over 18 hours.

b. For the initial amount $[\text{A}]_0 = 0.00500$ mol/L, if half of the initial amount reacts, we will have $[\text{A}]_t = 0.00250$ mol/L. Using the same equation and rate constant, we have

$$\frac{1}{0.00250 \text{ mol/L}} - \frac{1}{0.00500 \text{ mol/L}} = \left(3.07 \times 10^{-4} \frac{1}{\text{M} \cdot \text{s}}\right) \cdot t$$

$$400.\ \frac{\text{L}}{\text{mol}} - 200.\ \frac{\text{L}}{\text{mol}} = \left(3.07 \times 10^{-4} \frac{1}{\text{M} \cdot \text{s}}\right) \cdot t$$

$$200.\ \frac{\text{L}}{\text{mol}} = \left(3.07 \times 10^{-4} \frac{1}{\text{M} \cdot \text{s}}\right) \cdot t$$

The molarity units cancel, and we solve for the time:

$$t = 651{,}000 \text{ s}$$

which is more than seven days.

c. Notice that the time—the half-life—is much higher for the lower initial amount. This shows that the half-life for a second-order reaction is not a constant of the reaction, but rather depends on the initial amount.

The previous example shows that the term "half-life" can be applied to any order of reaction, not just first-order reactions. However, only for first-order reactions is the half-life independent of the initial amount, and a characteristic of the reaction. For any other order of reaction, a half-life *can* be defined, but will always include the initial amount in the expression. For example, for second-order reactions, the half-life $t_{1/2}$ can be defined as

$$t_{1/2} = \frac{1}{k \cdot [\text{A}]_0} \tag{20.22}$$

This equation shows (as did the previous example) that as the initial amount $[\text{A}]_0$ gets larger, the amount of time it takes for half of the reactant to react gets smaller. Such relationships are useful to synthetic and industrial chemists who are performing chemical processes.

There are a few other simple rate laws, and the integrations of those rate laws follow the same type of steps we used to find integrated rate laws for first- and second-order reactions. Rather than repeat such derivations, they will be left to the student. The discussion will be confined to some more interesting attributes of other rate laws. For example, a reaction following zeroth-order kinetics has a rate law of

$$-\frac{d[\text{A}]}{dt} = k \cdot [\text{A}]^0 = k \tag{20.23}$$

That is, the rate of disappearance of A is a constant, the zeroth-order rate constant. These types of reactions are rare, but they do occur: for example, conversion of ingested ethyl alcohol (CH_3CH_2OH) into acetaldehyde (CH_3CHO) in the body follows zeroth-order kinetics.

We can consider equation 20.23 in several equivalent ways. Since the rate of disappearance of reactant A is a constant, a plot of $[\text{A}]_t$ versus time is a straight

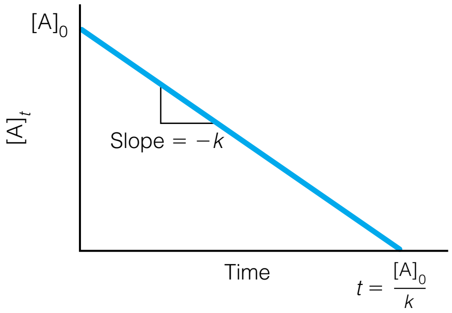


Figure 20.4 For a zeroth-order reaction, a plot of $[A]_t$ versus time gives a straight line with a slope of $-k$, a y-intercept of $[A]_0$, and an x-intercept of $[A]_0/k$. This is characteristic of a zeroth-order reaction; no other order reaction gives a straight line when plotting $[A]_t$ versus time. This is also the only graph (for simple rate laws) that has an x-intercept.

line, as shown in Figure 20.4. Also, we can integrate equation 20.23 to get the integrated zeroth-order rate law

$$[A]_0 - [A]_t = k \cdot t \tag{20.24}$$

where t represents elapsed time.

Also, we can again determine an expression for the half-life for a zeroth-order reaction. It is

$$t_{1/2} = \frac{[A]_0}{2 \cdot k} \tag{20.25}$$

Note that the half-life depends on the initial amount, as expected. You need to recognize something else about a zeroth-order reaction: after two half-lives, *all of reactant A is gone and the reaction is finished.* (This assumes that the reaction remains zeroth-order at all concentrations and actually goes to completion.) Thus, a straight-line plot of a zeroth-order reaction will have an x-intercept in addition to a y -intercept.

So far, we have focused on reactions whose rate law can easily be written in terms of a single reactant. Many reactions have rates that are dependent on more than one concentration, and in the extreme can be very complex. The simplest of these can be written for the two-species reaction

$$aA + bB \longrightarrow \text{products}$$

and we can write the rate(s) as

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = k \cdot [A][B] \tag{20.26}$$

This reaction is first-order with respect to A and first-order with respect to B, but is overall a second-order reaction. To determine the integrated form of this rate law, we will have to take a double integral over concentrations of A and B. We present only the final result:

$$\frac{1}{b[A]_0 - a[B]_0}\left(\ln\frac{[B]_0}{[A]_0} - \ln\frac{[B]_t}{[A]_t}\right) = k \cdot t \tag{20.27}$$

This equation can also be written as a straight-line equation (although some rearrangement is needed), and by plotting the log of the ratio $[B]_t/[A]_t$ versus time, one can determine the rate constant k in terms of the initial amounts as well as the coefficients of the balanced reaction.

Rate laws can get very complicated, very quickly. (Simply browse through a textbook on kinetics to get an idea of how complex some of them are.) Experimentally, it is difficult to determine rate laws of complicated reactions having many concentration terms in the rate law expression unless the experimenter resorts to some simplifying tactics. One such tactic is to perform the reaction with a large excess of all but one of the reactants. Consider a reaction that has a rate law

$$\text{rate} = k[A]^m[B]^n$$

If the reactant B were present in very large excess with respect to A, then during the initial course of the reaction the concentration of B does not change very much and can be approximated as constant. Any change in the rate of the reaction is thus related to changes in [A]. We have

$$\underbrace{\text{rate}}_{\text{measured}} = \underbrace{k}_{\text{constant}} \cdot [A]^m \cdot \underbrace{[B]^n}_{\sim\text{ constant}}$$

We can combine the two constants on the right side of the equation into a single variable, labeled k':

$$\text{rate} \approx k'[\text{A}]^m$$

The constant k' is called the *pseudo rate constant* for the rate law. Under these experimental conditions, it is much easier to determine the rate law and the rate constant for this simpler rate expression.

Probably the most common usage of this tactic is where the order m equals 1, so that the rate of the reaction follows the approximate expression

$$\text{rate} = k'[\text{A}] \qquad \textbf{(20.28)}$$

Reactions that are intentionally set up this way are said to be following *pseudo first-order kinetics*, and the constant k' is the *pseudo first-order rate constant.* Again, in reality a reaction might have some other, more specific rate law. Only under special conditions [that is, with a high, almost unchanging concentration of the other reactant(s)] will the reaction show pseudo first-order kinetics.

Note too that the pseudo first-order rate constant k' has different units than the true rate constant k of the same reaction. The units on k' are always 1/s, whereas the units on k depend on the entire rate law. The specific numerical value of k' depends on how high the concentration of the excess reactant is, as the following example shows.

Example 20.6

The following data are collected for a chemical reaction at constant temperature, arbitrarily A + B → products.

[A] (M)	[B] (M)	**Initial rate** ($\times 10^{-7}$ **M/s**)
0.00636	0.00384	2.91
0.0108	0.00384	4.95
0.00636	0.00500	4.95

a. Determine the rate law and the value of the rate law constant k.
b. Estimate the value of k', the pseudo first-order rate law constant, if [B] = 0.500 M and all other conditions are the same.

Solution

a. By performing an analysis like the one shown in Example 20.2, you should be able to see that the rate law is

$$\text{rate} = k \cdot [\text{A}]^1[\text{B}]^2$$

To get the order with respect to B, you have to use logarithms because the concentrations and rates are not in exact (or even close!) whole-number ratios. When the first and second trials are used, one gets

$$\frac{4.95 \times 10^{-7}\ \text{M/s}}{2.91 \times 10^{-7}\ \text{M/s}} = \frac{(0.00500\ \text{M})^n}{(0.00384\ \text{M})^n}$$

$$1.701 = (1.302)^n$$

In order to determine n, take the logarithm of both sides:

$$\log(1.701) = n \cdot \log(1.302)$$

$$0.2307 = n \cdot (0.1146)$$

$$n = \frac{0.2307}{0.1146} = 2.01 \approx 2$$

In performing an experiment, exact whole-number ratios are difficult to guarantee, so calculations with logarithms are common. Evaluating the value of k using the first set of data:

$$2.91 \times 10^{-7}\ \frac{\text{M}}{\text{s}} = k \cdot (0.00636\ \text{M})^1(0.00384\ \text{M})^2$$

$$k = 3.103\ \frac{1}{\text{M}^2{\cdot}\text{s}}$$

b. To evaluate k', we need to recognize that the pseudo first-order rate constant can be approximated by combining the k and the $[\text{B}]^2$ terms. If we are given $[\text{B}] = 0.500$ M, then

$$k' = \left(3.103\ \frac{1}{\text{M}^2{\cdot}\text{s}}\right)(0.500\ \text{M})^2$$

$$k' = 0.776\ \frac{1}{\text{s}}$$

where the units for k' work out as expected. The pseudo first-order rate law would be, under these conditions,

$$\text{rate} = \left(0.776\ \frac{1}{\text{s}}\right) \cdot [\text{A}]$$

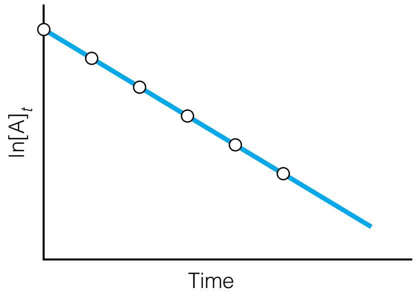


Figure 20.5 If a perfect kinetics experiment were performed on a first-order reaction, your graph might look like this: all data points on a line. However, reality isn't usually this perfect: see Figures 20.6 and 20.7.

To finish this section, let us briefly consider some of the experimental considerations of rate law determinations. It is typical in deriving physical chemical expressions to presume that our chemical system will follow the predictions of these equations (in these cases, $[\text{A}]_t$) perfectly. For an ideal kinetics experiment, one would expect to get a plot like that in Figure 20.5 for a first-order reaction.

However, in reality the data are rarely so perfect. In a real experiment in a real laboratory, a researcher might get some scatter in the plotted data. Table 20.1 gives some values of concentrations versus time, which are plotted in Figure 20.6. In this case, it might be obvious that a straight line is the best fit to the experimental data and that the reaction follows first-order kinetics, even though there is some scatter in the plotted points. However, an experimenter should be careful: consider plotting the same data as if it related to a second-order reaction. This is shown in Figure 20.7. For the short

Table 20.1 Kinetic data for Figures 20.6 and 20.7

Time (min)	$[\text{A}]_t$	$\ln[\text{A}]_t$	$1/[\text{A}]_t$
0	2.719	1.000	0.3678
1	2.612	0.9601	0.3829
2	2.586	0.9501	0.3867
3	2.509	0.9199	0.3985
4	2.459	0.8997	0.4066

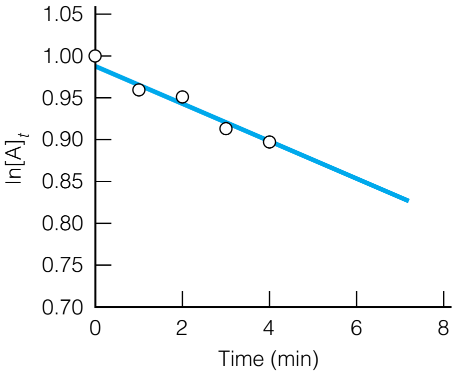


Figure 20.6 Data from Table 20.1 are plotted to see if the reaction follows first-order kinetics. Note the scatter in the experimental data that suggests that the fit to a straight line, in this case, is possible but not convincing. Compare with Figure 20.7.

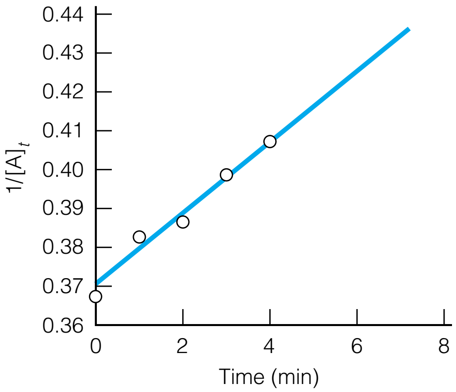


Figure 20.7 Data from Table 20.1 are plotted to see if the reaction follows second-order kinetics. Note the scatter in the experimental data that suggests that the fit to this straight line also does not convince us that this is a second-order reaction. Compare with Figure 20.6.

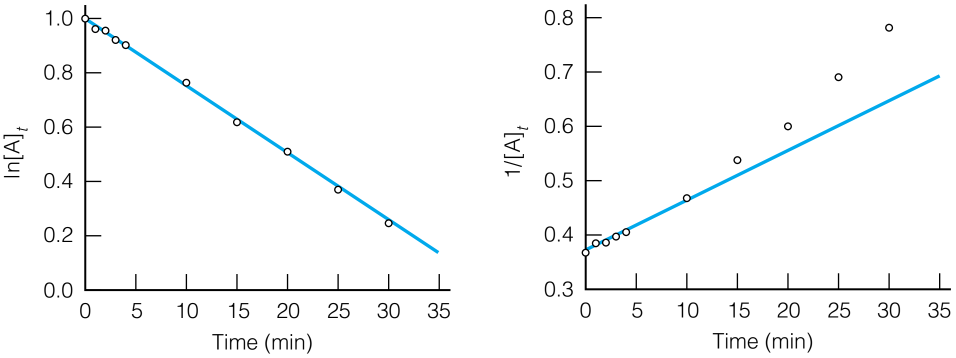


Figure 20.8 If the time of the measurements is extended (using data from Table 20.1a), it becomes clear that a first-order plot fits the data better than a second-order plot: a straight-line fit is more obvious for the first-order plot over longer periods of time. In experimental kinetics, it is extremely important to extend an experiment to a long enough time that the appropriate straight line—and therefore the correct order of the reaction—is determined conclusively.

time scale considered, neither plot makes a good case for a particular order of kinetics.

A good experimenter exploring the kinetics of an unknown reaction needs to apply care not only in the experimental measurements (here, the $[A]_t$ measurements) but also in the definition of the experimental conditions: the initial [A], initial [B], elapsed time, and so on. Understand that these conditions are chosen by the experimenter. If we include data from Table 20.1a, we can extend the time of the experiment and try to make an obvious fit to a straight line. Figure 20.8 shows plots of all the data. Now it should be more obvious what the rate law of the reaction is.

Table 20.1a Additional kinetic data for Figure 20.8

Time (min)	$[A]_t$	$\ln [A]_t$	$1/[A]_t$
10	2.138	0.7599	0.4677
15	1.855	0.6179	0.5390
20	1.664	0.5092	0.6011
25	1.448	0.3702	0.6907
30	1.276	0.2437	0.7835

20.4 Equilibrium for a Simple Reaction

Kinetics describes how reactions proceed, but we should understand from thermodynamics that virtually all reactions do not proceed to completion. Instead, in time a reverse reaction begins to occur, and when the rate of the reverse reaction equals the rate of the forward reaction, net change ceases and the system is at a *dynamic equilibrium.* Although we have stated previously that thermodynamics and kinetics are separate considerations, the previous statement—that the rate of forward reaction equals the rate of reverse reaction for a system at equilibrium—suggests that there are some connections between kinetics and thermodynamics.

In our discussion of initial rates, we were implicitly confining ourselves to short periods of time near the beginning of the reaction. That is, we assumed ξ was small. For equilibrium conditions, however, we need to consider a different time regime, that where ξ approaches its maximum value. What this implies is that a reverse chemical process will become important in our understanding of how concentrations are changing. This reverse reaction is an additional consideration that we have so far ignored.

Consider the following simple chemical process:

$$\mathrm{A} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{B} \tag{20.29}$$

Here, k_f is the rate constant for the forward reaction and k_r is the rate constant for the reverse reaction. Furthermore, we will assume that each reaction is first-order with respect to its reactant, and that the initial amount of reactant A is given by $[\mathrm{A}]_0$ while $[\mathrm{B}]_0 = 0$.

The rate of change of concentration of A is given by

$$\frac{d[\mathrm{A}]}{dt} = -k_\mathrm{f}[\mathrm{A}] + k_\mathrm{r}[\mathrm{B}] \tag{20.30}$$

The first term on the right is negative because it relates the *disappearance* of A, and the second term is positive because it contributes to an *increase* in A. At any time t, we can modify the concentrations in equation 20.30 to show that the overall rate depends on the concentrations of A and B at any time:

$$\frac{d[\mathrm{A}]_t}{dt} = -k_\mathrm{f}[\mathrm{A}]_t + k_\mathrm{r}[\mathrm{B}]_t \tag{20.31}$$

Now, $[\mathrm{A}]_t$ and $[\mathrm{B}]_t$ imply that the rate is dependent on the instantaneous concentrations of A and B at any time. Notice that the rate is also written in terms of the instantaneous concentration $[\mathrm{A}]_t$. Because of the 1 : 1 stoichiometry in the balanced chemical reaction and the law of conservation of mass, there is a relationship between [A] and [B] at any time:

$$[\mathrm{B}]_t + [\mathrm{A}]_t = [\mathrm{A}]_0 \quad \text{or} \quad [\mathrm{B}]_t = [\mathrm{A}]_0 - [\mathrm{A}]_t$$

Substituting for $[\mathrm{B}]_t$ and rearranging:

$$\frac{d[\mathrm{A}]}{dt} = -k_\mathrm{f}[\mathrm{A}]_t + k_\mathrm{r}([\mathrm{A}]_0 - [\mathrm{A}]_t) = k_\mathrm{r}[\mathrm{A}]_0 - (k_\mathrm{r} + k_\mathrm{f})[\mathrm{A}]_t \tag{20.32}$$

Although this equation may look complicated, it is simply a first-order differential equation in one variable, $[\mathrm{A}]_t$. It has a solution that involves exponential functions, and the equations that satisfy this differential equation (that is, the "solutions" to the differential equation) are

$$[\mathrm{A}]_t = \frac{[\mathrm{A}]_0}{(k_\mathrm{f} + k_\mathrm{r})}\,(k_\mathrm{r} + k_\mathrm{f} \cdot e^{-(k_\mathrm{f}+k_\mathrm{r})t}) \tag{20.33}$$

It is actually fairly easy to show that at the beginning of the process, when the reverse reaction's effect is negligible, the above equation reduces to

$$[\mathrm{A}]_t = [\mathrm{A}]_0 \cdot e^{-k_\mathrm{f} \cdot t}$$

This is equivalent to equation 20.15.

Another integrated form of the rate law in equation 20.32 has the form

$$\ln\left(\frac{[\mathrm{A}]_0 - [\mathrm{A}]_\mathrm{eq}}{[\mathrm{A}]_t - [\mathrm{A}]_\mathrm{eq}}\right) = (k_\mathrm{f} + k_\mathrm{r}) \cdot t \tag{20.34}$$

which has the form of a straight line—plotting the logarithm term in equation 20.34 versus time—with a slope of $(k_\mathrm{f} + k_\mathrm{r})$ and a y-intercept of zero. Again, at the limit of initial reaction conditions this plot will turn into the expected plot for a first-order reaction, but now we are extending the plot to consider longer time periods in which the reverse reaction has an effect on $[\mathrm{A}]_t$.

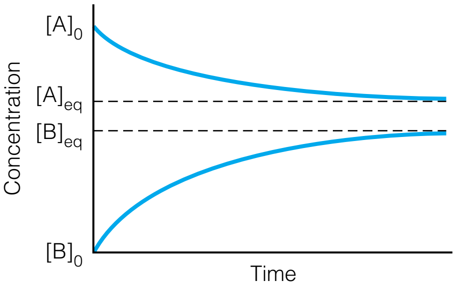


Figure 20.9 As a reaction approaches equilibrium, the amounts of reactant, $[\mathrm{A}]_t$, and product, $[\mathrm{B}]_t$, approach their equilibrium values (which depend on the reaction). Compare this plot of $[\mathrm{A}]_t$ with Figure 20.1: at long values for time, the plots differ. This plot of $[\mathrm{A}]_t$ follows equation 20.33, not equation 20.15.

Figure 20.9 shows a plot of $[\mathrm{A}]_t$ that illustrates an expected behavior: an exponential decrease toward some asymptotic minimum. At the same time, the amount of the product $[\mathrm{B}]_t$ is shown as *increasing* toward some asymptotic maximum. The actual asymptotic values of $[\mathrm{A}]_t$ and $[\mathrm{B}]_t$ are dependent on the initial value $[\mathrm{A}]_0$ as well as the values of k_f and k_r.

But the asymptotic values of $[\mathrm{A}]_t$ and $[\mathrm{B}]_t$ over time are the expected equilibrium concentrations of A and B, labeled $[\mathrm{A}]_\mathrm{eq}$ and $[\mathrm{B}]_\mathrm{eq}$. There must be some connection, then. The connection is simple. We define an equilibrium constant K for this simple reaction as the quotient of the concentration of the products and the reactants:

$$\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} \equiv K \tag{20.35}$$

With this definition and the relationships between the concentrations of A and B, it can be shown from equation 20.33 that as $t \to \infty$:

$$[\mathrm{A}]_{\mathrm{eq}} = \frac{k_{\mathrm{r}}}{(k_{\mathrm{f}} + k_{\mathrm{r}})} \cdot [\mathrm{A}]_0$$

It follows that for this simple reaction,

$$[\mathrm{B}]_{\mathrm{eq}} = 1 - [\mathrm{A}]_{\mathrm{eq}} = \frac{k_{\mathrm{f}}}{(k_{\mathrm{f}} + k_{\mathrm{r}})} \cdot [\mathrm{A}]_0$$

$$K = \frac{k_{\mathrm{f}}}{k_{\mathrm{r}}} \tag{20.36}$$

The last equation is especially noteworthy for its simplicity (and its potential usefulness), although all three equations above are applicable to first-order or pseudo first-order reactions.* These three expressions (and the concepts used to derive them) represent one connection between kinetics and thermodynamics. Other expressions can be derived for higher-order reactions, but they all mimic similar ideas in mass conservation and the mathematics of differential equations.

20.5 Parallel and Consecutive Reactions

The previous section used a simple reaction, A → B, to introduce a connection that does exist between kinetics and thermodynamics. Many chemical equations are not this simple. For some reactions, more than one product is possible; these are *parallel reactions.* And commonly, in other cases, the product of the first reaction is the reactant of a second reaction, which may in turn be the reactant of another reaction, and so on. These are examples of *consecutive reactions.*

A simple parallel reaction can be illustrated as

$$\begin{tikzcd} \mathrm{A} \arrow[r, "k_1"] \arrow[d, "k_2"'] & \mathrm{B} \\ \mathrm{C} & \end{tikzcd}$$

in which some reactant A can react to form two possible products, labeled B or C. The rate constants for each individual reaction are labeled k_1 and k_2, respectively. As an example, the thermal decomposition of many small hydrocarbons like CH_4 can occur via several pathways simultaneously, constituting a set of parallel (also called *competing* or *concurrent*) reactions.

Consider a system in which the rate laws of both reactions are first-order with respect to A. If we start such a reaction with only A present, the initial rate of disappearance of A can be written as

---

*Equation 20.36 also applies to any forward-and-reverse reactions whose orders are equal to the stoichiometric coefficients of the reactants for each process. We won't be considering any examples of this application here.

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}]_t + k_2[\mathrm{A}]_t = (k_1 + k_2) \cdot [\mathrm{A}]_t \tag{20.37}$$

Because equation 20.37 has only one variable (the concentration of A), it can be integrated just like any other first-order rate law. In doing so (and in making the same assumptions that the initial time is set to zero so that the variable t stands for *elapsed* time), we get

$$[\mathrm{A}]_t = [\mathrm{A}]_0 \cdot e^{-(k_1+k_2)t} \tag{20.38}$$

This relates the concentration of A over time, and should be no great surprise. The initial rates of appearances of the two products, B and C, are

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}]_t$$

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{A}]_t$$

Substituting for $[\mathrm{A}]_t$ from equation 20.38, we get

$$\frac{d[\mathrm{B}]}{dt} = k_1 \cdot [\mathrm{A}]_0 \cdot e^{-(k_1+k_2)t} \tag{20.39}$$

$$\frac{d[\mathrm{C}]}{dt} = k_2 \cdot [\mathrm{A}]_0 \cdot e^{-(k_1+k_2)t} \tag{20.40}$$

These expressions can be integrated in order to determine the concentrations of B and C over time. If it is assumed that the initial amounts of B and C are zero at some initial time (that is, $[\mathrm{B}]_t = [\mathrm{C}]_t = 0$ at $t = 0$), these two equations can be integrated to yield

$$[\mathrm{B}]_t = \frac{k_1 \cdot [\mathrm{A}]_0}{k_1 + k_2} \cdot (1 - e^{-(k_1+k_2)t}) \tag{20.41}$$

$$[\mathrm{C}]_t = \frac{k_2 \cdot [\mathrm{A}]_0}{k_1 + k_2} \cdot (1 - e^{-(k_1+k_2)t}) \tag{20.42}$$

Both of these concentrations depend on negative exponentials, but in these cases the negative exponential is subtracted from 1. Therefore, as time increases and the negative exponential gets smaller and smaller, the difference gets larger and larger, and [B] and [C] increase as the elapsed time increases. Figure 20.10 shows the behavior of $[\mathrm{A}]_t$, $[\mathrm{B}]_t$, and $[\mathrm{C}]_t$ for a given set of rate constants.

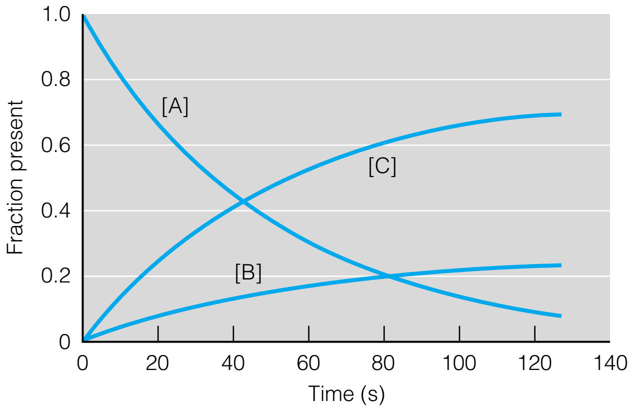


Figure 20.10 Plots of $[\mathrm{A}]_t$, $[\mathrm{B}]_t$, and $[\mathrm{C}]_t$ versus time for two parallel reactions in which $k_1 = 0.005\ \mathrm{s}^{-1}$ and $k_2 = 0.015\ \mathrm{s}^{-1}$. The initial concentrations of B and C are dictated by the relative magnitudes of the two rate constants. For a plot over a long period of time in which equilibria are established, see Figure 20.11.

Equations 20.41 and 20.42 may look a bit complicated, but the ratio of $[\mathrm{B}]_t$ and $[\mathrm{C}]_t$ has a very simple expression:

$$\frac{[\mathrm{B}]_t}{[\mathrm{C}]_t} = \frac{k_1}{k_2} \tag{20.43}$$

This expression is valid for any time t, as long as the reverse reactions are negligible.

When the reactions approach equilibrium, our analysis of the situation must change. Near equilibrium, product converts back to reactant, which can then convert over to product again. But there is no requirement that the reactant molecule react to make the same product! (That is, molecules do not have memory.) We need to consider the following scheme:

$$\begin{tikzcd}
\mathrm{A} \arrow[r, shift left, "k_1"] \arrow[d, shift right, "k_2"'] & \mathrm{B} \arrow[l, shift left, "k_{-1}"] \\
\mathrm{C} \arrow[u, shift right, "k_{-2}"'] &
\end{tikzcd}$$

Not only have we defined forward rate constants k_1 and k_2, but we also define reverse rate constants k_{-1} and k_{-2}. According to the previous section, we can also define equilibrium constants for each reaction, K_1 and K_2, as

$$K_1 = \frac{k_1}{k_{-1}}$$

$$K_2 = \frac{k_2}{k_{-2}}$$

Without presenting the derivation, we simply state that at equilibrium (that is, as $t \to \infty$), the concentrations of products and reactant are

$$\begin{aligned}
[\mathrm{A}]_{\mathrm{eq}} &= \frac{[\mathrm{A}]_0}{K_1 + K_2 + 1} \\
[\mathrm{B}]_{\mathrm{eq}} &= \frac{K_1 \cdot [\mathrm{A}]_0}{K_1 + K_2 + 1} \\
[\mathrm{C}]_{\mathrm{eq}} &= \frac{K_2 \cdot [\mathrm{A}]_0}{K_1 + K_2 + 1}
\end{aligned} \tag{20.44}$$

Additionally,

$$\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{C}]_{\mathrm{eq}}} = \frac{K_1}{K_2} \tag{20.45}$$

Equation 20.45 can be considered a special case of equation 20.43. At the limit of small times, the effects of the reverse reactions are negligible and equation 20.43 is applicable. Only in the case of long times, where reverse reactions have an appreciable effect on concentrations and equilibria are being established, does equation 20.45 become applicable. However, there is no reason to presume that the ratios $[\mathrm{B}]_t/[\mathrm{C}]_t$, the product ratio at some intermediate time, and $[\mathrm{B}]_{\mathrm{eq}}/[\mathrm{C}]_{\mathrm{eq}}$, the product ratio at "infinite time," are the same.

When two parallel reactions begin initially, the reaction that goes faster is the one with the larger rate constant (assuming that both reactions are simple first-order reactions). Therefore, the specific ratio of products *initially*, given by $[\mathrm{B}]_t/[\mathrm{C}]_t$, will be given by the ratio of the forward rate constants k_1/k_2. Because the initial product ratio is determined by the kinetics of the forward reactions (that is, equation 20.43), we say that the ratio of products is *kineti-*

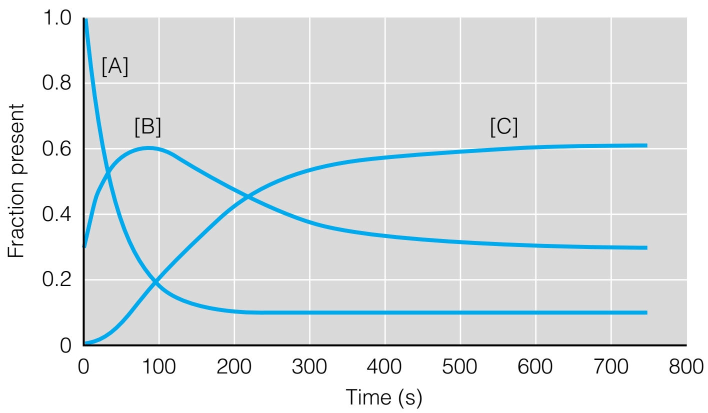


Figure 20.11 Plots of $[A]_t$, $[B]_t$, and $[C]_t$ for a long period of time in which equilibria can be established. Now the relative concentrations of B and C are dependent on the equilibrium constants of the individual reactions, not just the rate constants of the two forward parallel reactions.

cally controlled. However, over long time intervals, the ultimate ratio of products will depend on the individual equilibrium constants of the separate reactions. Since equilibrium constants are ultimately related to the thermodynamics of the reaction, we say that the ratio of products under these conditions is *thermodynamically controlled.*

The ratio of products at any one instant may be completely different depending on whether the ratio is dictated by kinetic control or thermodynamic control. For example, consider parallel reactions in which $k_1 = 1 \times 10^{-2}$ and $k_{-1} = 1 \times 10^{-4}$ (which relate to product B) while $k_2 = 1 \times 10^{-3}$ and $k_{-2} = 1 \times 10^{-7}$ (which relate to product C). The two equilibrium constants K_1 and K_2, are 100 and 10,000, respectively.

Initially, because k_1 is 10 times larger than k_2, more of product B is produced than product C. We say that B is the *kinetically favored product.* However, as equilibria are established over a long period of time, the amount of product C is much larger because its equilibrium favors products much more than the B product is favored by its independent equilibrium. We say that product C is the *thermodynamically favored product.* Figure 20.11 shows a graph of how product B is produced in larger quantities at first, and how this changes over longer periods of time as equilibria are established. If a chemical producer is interested in product B, the kinetically favored product, a way to remove B from the system would need to be developed, or else B will re-react and form C, the thermodynamically favored product.

There are many cases of *consecutive reactions,* in which the product of a first reaction is the reactant (or one of the reactants) of a second reaction, and so on. A simple consecutive reaction scheme can be represented as

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Radioactive decay series are good examples of consecutive reactions. Assuming (as is usually the case) that a system starts out with only A present and no B or C, the rates of change of concentration of the three species in the above sequence are

$$-\frac{d[A]}{dt} = k_1[A]_t$$

$$\frac{d[B]}{dt} = k_1[A]_t - k_2[B]_t \tag{20.46}$$

$$\frac{d[C]}{dt} = k_2[B]_t$$

The rate of change in concentrations of A and C should appear reasonable from inspection of the sequential reaction. The rate of change of concentration of B is a combination of two effects: an increase in [B] due to formation *from* A, and a decrease in [B] due to the formation *of* C. The positivity and negativity of each term reflects the corresponding increase or decrease.

The three equations 20.46 can be integrated to yield

$$[\mathrm{A}]_t = [\mathrm{A}]_0 \cdot e^{-k_1 t}$$

$$[\mathrm{B}]_t = \frac{k_1 \cdot [\mathrm{A}]_0}{k_2 - k_1} \cdot (e^{-k_1 t} - e^{-k_2 t}) \tag{20.47}$$

$$[\mathrm{C}]_t = [\mathrm{A}]_0 \left[1 + \frac{1}{k_1 - k_2}(k_2 \cdot e^{-k_1 t} - k_1 \cdot e^{-k_2 t}) \right]$$

where again, t represents the elapsed time and $[\mathrm{A}]_0$ is the original amount of reactant A in the system. (Remember, we are assuming that the original amounts of B and C are zero.) The expression for $[\mathrm{A}]_t$ should look familiar; it is exactly the same as equation 20.15.

However, the expressions for $[\mathrm{B}]_t$ and $[\mathrm{C}]_t$ are more complicated. Both of them, as a matter of fact, depend on both rate constants for both reactions. Furthermore, they also depend on the differences in the rate constants (indicated by the $k_2 - k_1$ and $k_1 - k_2$ terms in the denominators of the expressions). If, for example, the second reaction is much slower than the first reaction (that is, $k_1 \gg k_2$), there is an initial buildup of product B as shown by the left part of Figure 20.12. Only over long periods of time will product B eventually react to form the final product C, which is illustrated on the right part of Figure 20.12. (Although there may be some tendency to refer to B as the kinetically favored product and C as the thermodynamically favored product, this is not an accurate parallel.)

When $k_1 \ll k_2$, the second reaction is much faster than the first one and the penultimate product B reacts to the ultimate product C almost as fast as B itself is formed. The amounts of products over time are illustrated by Figure 20.13. Notice that very little of B is present at any time. The reaction system will remain this way unless a large amount of B is favored by the equilibria of the two reactions.

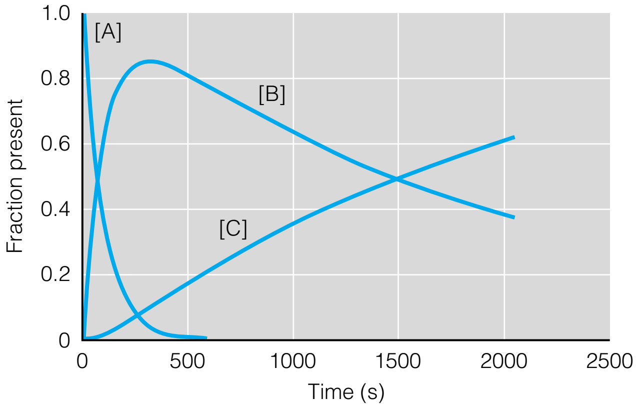


Figure 20.12 For consecutive reactions in which k_1 is much greater than k_2, there is a short-term buildup of the intermediate product, B. But over longer periods of time, the final product C is formed. In this plot, $k_1 = 0.01\ \mathrm{s}^{-1}$ and $k_2 = 0.0005\ \mathrm{s}^{-1}$.

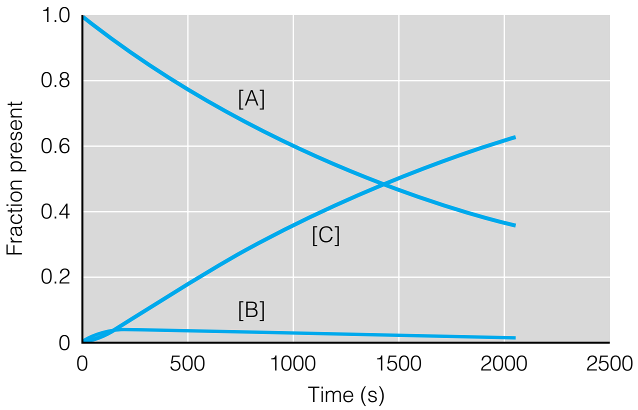


Figure 20.13 For consecutive reactions in which k_1 is much smaller than k_2, there is very little initial buildup of the intermediate product, B. The final product, C, is formed almost immediately. In this plot, $k_1 = 0.0005\ \text{s}^{-1}$ and $k_2 = 0.01\ \text{s}^{-1}$. Compare this to Figure 20.12.

Example 20.7

Kinetics of consecutive reactions are easily applicable to nuclear decay processes, in which a parent isotope produces a radioactive daughter isotope that also decays. (In fact, in the early twentieth century, such sequential processes were a major complicating factor in trying to understand this new phenomenon.) One such example is

$$^{210}_{83}\text{Bi} \xrightarrow{t_{1/2,1}} {}^{210}_{84}\text{Po} \xrightarrow{t_{1/2,2}} {}^{206}_{82}\text{Pb}$$

which are the last two steps in the radioactive decay series starting with $^{238}_{92}\text{U}$ and ending in the nonradioactive isotope of Pb. (It is sometimes called the *4n + 2 series* because all of the mass numbers of the isotopes involved can be represented by that general equation.) The half-lives, $t_{1/2,1}$ and $t_{1/2,2}$, are 5.01 days and 138.4 days, respectively. Comment on the relative amounts of ^{210}Bi, ^{210}Po, and ^{206}Pb over time.

Solution

The presentation of this example is potentially misleading because the problem gives half-lives, not rate constants! Equation 20.17 should be consulted for the relationship between $t_{1/2}$ and k:

$$t_{1/2} = \frac{0.693}{k}$$

Using this, and keeping track of two different half-lives and their related rate constants using subscripts, we get

$$t_{1/2,1} = 5.01\ \text{d} = 4.33 \times 10^5\ \text{s}$$

$$t_{1/2,2} = 138.4\ \text{d} = 1.196 \times 10^7\ \text{s}$$

(where the half-lives have been converted into standard units). Therefore

$$k_1 = \frac{0.693}{4.33 \times 10^5\ \text{s}} = 1.60 \times 10^{-6}\ \text{s}^{-1}$$

$$k_2 = \frac{0.693}{1.196 \times 10^7\ \text{s}} = 5.79 \times 10^{-8}\ \text{s}^{-1}$$

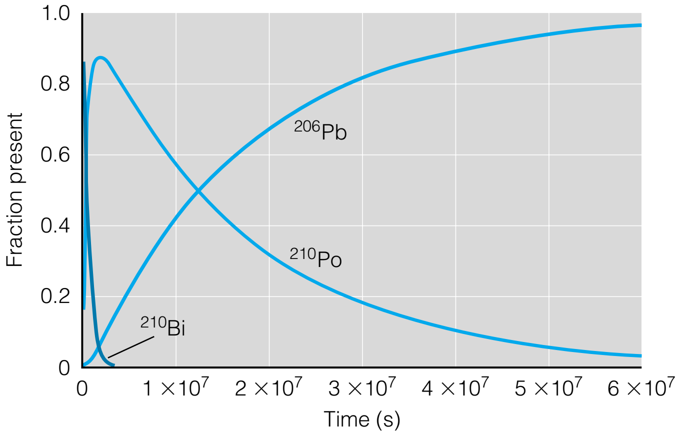


Figure 20.14 See Example 20.7. This plot shows the concentrations of ^{210}Bi, ^{210}Po, and ^{206}Pb over time. Note the "temporary" buildup of ^{210}Po, which does start at 0. Note that the *x*-axis is in units of seconds, but in this example the right side of the plot is equivalent to a time of 1.9 years.

Here, we can see that k_1 is much larger than k_2 (that is, 10^{-6} is two orders of magnitude higher than 10^{-8}), so we might expect that there would be a "momentary" buildup of polonium. Then, as time proceeds, the amount of polonium would decrease as it decays to the stable lead isotope. Figure 20.14 shows a plot of what ultimately happens to 1.00 gram of ^{210}Bi.

The complete $4n + 2$ series has 14 nuclear reactions between ^{238}U and ^{206}Pb, with a total of 15 nuclear species. Can you imagine the 15 mathematical expressions that give their concentrations over time?

20.6 Temperature Dependence

The rates of chemical reactions are strongly affected by temperature. This is one reason why most declarations of rate constants include a temperature at which that constant is valid. Common temperatures are 25°C (a common standard temperature) and 37°C ("normal" human body temperature). Because temperature is an obvious thermodynamic variable, this section considers another relationship between thermodynamics and kinetics.

Perhaps the most straightforward relationship between temperature and rate constants was suggested by Svante Arrhenius (Figure 20.15) in 1889. He used a thermodynamic approach in the form of an analogy. According to an expression known as the van't Hoff equation (*not* the van't Hoff equation from osmotic pressure considerations), the temperature variation in the equilibrium constant of a process is

$$\frac{\partial(\ln K)}{\partial(1/T)} = -\frac{\Delta_{\text{rxn}}H}{R} \qquad \textbf{(20.48)}$$

where $\Delta_{\text{rxn}}H$ is the change in enthalpy of the reaction and R is the ideal gas law constant. Arrhenius proposed an analogous equation by suggesting an "equilibrium" between reactant molecules and some transition species that is higher in energy (that is, less stable) than the reactants. The energy difference is called the *energy of activation* or, more simply, the *activation energy* of the reaction. The "equilibrium constant" of this so-called equilibrium is the rate


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Figure 20.15 Svante Arrhenius (1859–1927), a Swedish chemist who—among other things—came up with a simple relationship between the rate constant and the absolute temperature.

constant, k, of the reaction. Using the symbol E_A for activation energy, equation 20.48 becomes

$$\frac{\partial(\ln k)}{\partial(1/T)} = -\frac{E_A}{R}$$

Rearranging:

$$\partial(\ln k) = -\frac{E_A}{R}\,\partial\left(\frac{1}{T}\right)$$

Now both sides of the equation can be integrated:

$$\ln k = -\frac{E_A}{RT} + (\text{integration constant}) \qquad \textbf{(20.49)}$$

It is common to rewrite equation 20.49 by taking the exponential of both sides of the expression:

$$k = e^{-E_A/RT} \cdot e^{(\text{integration constant})}$$

The second exponential is some number; it is typically defined as A and the above equation is written as

$$k = A \cdot e^{-E_A/RT} \qquad \textbf{(20.50)}$$

This is called the *Arrhenius equation.* The constant A is sometimes referred to as the *pre-exponential factor.*

Estimates of E_A can be made using experimental values of rate constants determined at different temperatures. Or, if the activation energy is known, its value can be used to predict rate constants at new temperatures. Also, the natural logarithm of equation 20.50 can be taken to generate a new form of the Arrhenius equation:

$$\underbrace{\ln k}_{y} = \underbrace{\ln A}_{b} + \underbrace{\left(-\frac{E_A}{R}\right)}_{m} \cdot \underbrace{\frac{1}{T}}_{x} \qquad \textbf{(20.51)}$$

where the labels indicate how this form of the Arrhenius equation is written in the form of a straight line. Pre-exponential factors and activation energies can be estimated graphically.

Example 20.8

In a recent paper (Orkin et al., *J. Phys. Chem.*, 1997, 101: 174), rate constants were determined for the reaction between the hydroxyl radical and chlorobromomethane:

$$OH\cdot + CH_2BrCl \longrightarrow \text{products}$$

Data that were obtained included the following values of the rate constant k for the following temperatures:

T (K)	k [cm^3/(molecule·second)]
298	1.11×10^{-13}
313	1.34×10^{-13}
330	1.58×10^{-13}

Show graphically that the Arrhenius equation is followed (approximately, since these data are subject to experimental error), and determine A and E_A.

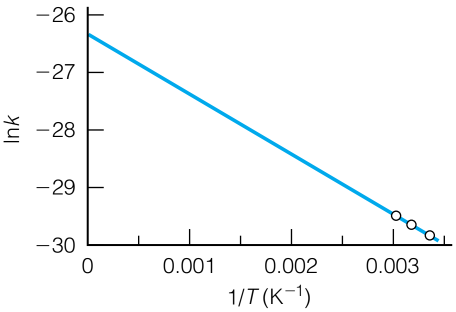

Figure 20.16 See Example 20.8. According to the plot of ln k versus $1/T$, the slope is equal to $-E_A/R$ and the y-intercept is equal to the natural logarithm of the pre-exponential constant. According to this plot, E_A is 8900 J/mol and A is about 3.78×10^{-12} cm^3/(molecule·second). See text for details.

Solution

First, we need to determine the values that we will be plotting: they aren't the values right from the table above! We need the following pairs of numbers:

ln k	$1/T$ (K^{-1})
−29.829	0.00336
−29.641	0.00319
−29.476	0.00303

See Figure 20.16 for a plot of ln k versus $1/T$. Although the three points do not all lie exactly on a straight line, it is a pretty good approximation of one (again, indicative of the natural variations in experimental measurements). The slope, which would equal $-E_A/R$, is about −1070, so by multiplying the ideal gas law constant R through, we get an estimate of E_A as 1070×8.314 J/mol = 8900 J/mol. (The temperature unit in the denominator of R is attached to the $1/T$ term.) The y-intercept of the plot is about −26.3, which is equal to ln A. Therefore, A is about 3.78×10^{-12} cm^3/(molecule·second). Notice that A has the same units as the given rate constants.

Example 20.9

Use the information derived from Example 20.8 to estimate the rate constant at 370 K. Compare it with the experimentally determined value of 2.10×10^{-13} cm^3/(molecule·second).

Solution

With an activation energy of 8900 J/mol, we can use the value of A and the given temperature and equation 20.50 directly:

$$k = A \cdot e^{-E_A/RT}$$

$$k = \left(3.8 \times 10^{-12} \frac{\text{cm}^3}{\text{molecule·second}}\right) \cdot \exp\left[-\frac{8900 \frac{\text{J}}{\text{mol}}}{\left(8.314 \frac{\text{J}}{\text{mol·K}}\right)(370 \text{ K})}\right]$$

Note how the units cancel in the exponential, as they should. Solving, we find that

$$k = 2.09 \times 10^{-13} \frac{\text{cm}^3}{\text{molecule·second}}$$

This is very close to the experimentally determined value, showing that the Arrhenius equation is a good model for this reaction.

If we have two sets of conditions, two versions of equation 20.51, labeled with 1 and 2 subscripts, can be subtracted to get the following expression:

$$\ln \frac{k_1}{k_2} = \left(-\frac{E_A}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \textbf{(20.52)}$$

which eliminates the need to know the pre-exponential factor A.

For some reactions, using the van't Hoff equation as the starting point to develop the Arrhenius equation is a little simplistic. Rather than assuming that

$$\left(\frac{\partial(\ln k)}{\partial(1/T)}\right) = -\frac{E_A}{R}$$

—that is, that this derivative has some constant value given by the expression $-E_A/R$—it is better to assume that the slope of the plot of ln k versus $1/T$ is dependent on temperature, also. That is, we also include a temperature term, so the equation becomes

$$\frac{\partial(\ln k)}{\partial(1/T)} = -\frac{E_A}{R} - m \cdot T \tag{20.53}$$

It is the convention to use a negative sign on this additional term. When we go through and do the rearrangements and integrations like we did for equation 20.50, we ultimately get

$$k = A \cdot T^m \cdot e^{-E_A/RT} \tag{20.54}$$

Defined like this, m is usually some negative number. For $m = 0$, equation 20.54 reduces into the Arrhenius equation.

How can we justify the Arrhenius equation beyond some energy difference between the reactants and a transition state? The pre-exponential factor, which is a constant for a given reaction (that is, it does not depend on temperature) must have a value that is dictated by the specifics of the reaction itself, like the nature of the reactants and how they interact on a molecular level.

What are the specific characteristics of a gas-phase molecular interaction that determine if the molecules react? One of the most obvious is the *number* of molecules that are colliding. The number of collisions is calculable from kinetic theory; we covered this topic starting in section 19.4. For example, at the end of that section we showed that the total number of collisions per second per unit volume, represented by Z, is given by

$$Z = \frac{\pi\rho_1\rho_2\left(\frac{d_1 + d_2}{2}\right)^2\sqrt{8kT}}{\sqrt{\pi\mu_{12}}} \tag{20.55}$$

where d_1 and d_2 are the diameters of gas particles in species 1 and 2, and μ is the reduced mass of two particles of those species. If we suggest that the effect of temperature changes is minor compared to the exponential term in the Arrhenius equation (that is, the $e^{-E_A/RT}$ term), and if the densities of the two species ρ_1 and ρ_2 are converted to concentrations and separated from the rest of the expression, then we can argue that the rest of the expression is approximately constant:

$$Z = \underbrace{\frac{\pi\left(\frac{d_1 + d_2}{2}\right)^2\sqrt{8kT}}{\sqrt{\pi\mu_{12}}}}_{\sim \text{ constant}} \times \rho_1\rho_2 \tag{20.56}$$

This one factor, a *collision frequency factor,* is one major contribution to the pre-exponential constant A.

A second contribution to the value of A is the orientation of the two reactant species with respect to each other, and what fraction of collisions are oriented properly so that bond rearrangement might occur (if the molecules have enough energy—but that's the consideration of the exponential term in the Arrhenius equation). Figure 20.17 shows an example of how we can argue for a *steric factor* as a contribution to the pre-exponential factor A. In one case, the

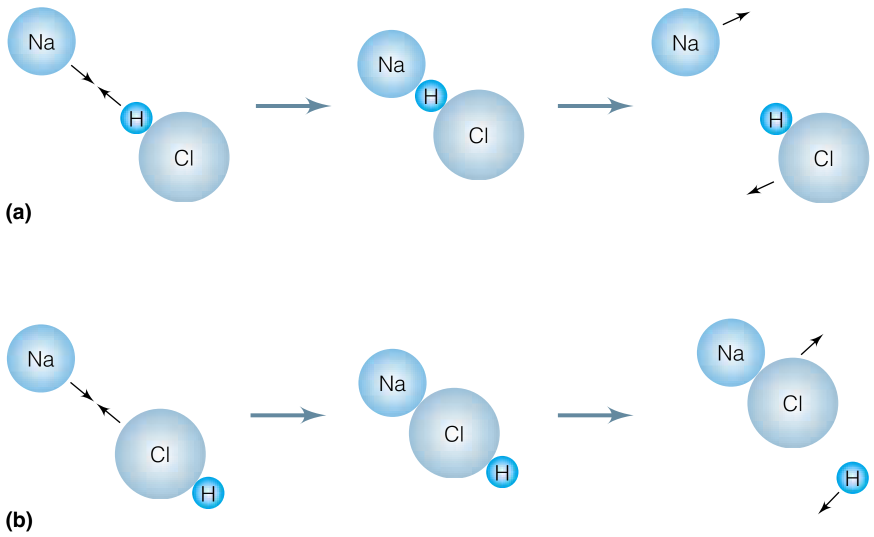

Figure 20.17 A simple example of how steric factors influence the probability of reactions occurring. (a) A sodium atom approaches an HCl molecule, but the orientations are not conducive for a reaction to occur, so after colliding they simply go on their way. (b) Here the orientation of the HCl is more conducive to reaction, so upon collision the Cl atom bonds with the Na atom and new product species are formed.

atoms are not arranged properly as they collide. In the other case, orientation factors are more favorable, and the reaction might proceed (if all other factors are favorable). Steric factors include not just the size of the collisional cross section (discussed in the previous chapter) but also considerations of reactant structure and geometry. A lot of current research, using molecular beams, is trying to determine the exact orientational relationships that promote a reaction that forms products. This description of simple chemical reactions is called *collision theory* and is a basic theoretical model of the kinetics of chemical reactions.

20.7 Mechanisms and Elementary Processes

Consider the following gas-phase reaction:

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (g) \tag{20.57}$$

Does the reaction really proceed like this at the molecular level? No, it does not: we recognize the above chemical reaction as simply the overall balanced chemical reaction. At the molecular level the individual reactant molecules are interacting in completely different ways; it's just that *overall* they react to yield the above balanced reaction.

The individual steps in any general chemical reaction are called *elementary processes*. The overall combination of sequential elementary processes, which collectively yields the balanced chemical reaction, is called the *mechanism* of the reaction. Although balanced chemical reactions are usually easy to determine, mechanisms of chemical reactions are much more difficult because the elementary processes are usually very quick and involve unstable species—transition states, for example—whose existences are difficult to determine, much less measure.

Because we cannot follow individual molecules from beginning (reactants) to end (products), it is very difficult to *prove* a mechanism for a chemical reaction. However, we can collect experimental evidence to *support* a proposed mechanism, or to show that some proposed mechanism is incorrect. (Thus the scientific axiom that any multitude of experiments can suggest that a hypothesis is correct, but only one experiment is needed to show that a hypothesis is incorrect.) Experimental techniques used to try to support a proposed mechanism include stopped-flow experiments for solution-phase chemistry and ultrafast (on a femtosecond timescale; a femtosecond is 10^{-15} second) laser spectroscopy for gas-phase reactions. We will not dwell on such techniques here; rather, we will focus on the elementary processes that such experiments might study.

For example, in the reaction of hydrogen and oxygen gases, the first elementary process in the overall reaction might be

$$H_2 + O_2 \longrightarrow 2OH\cdot \qquad \textbf{(20.58)}$$

That is, the two diatomic molecules collide in space and rearrange to form two new molecules, OH. Notice that this is *not* the hydroxide ion! It is a combination of one oxygen atom and one hydrogen atom, and as an uncharged diatomic molecule it has an odd number of electrons. Such odd-electron species are rare in main-group compounds. Typically, odd-electron molecules are reactive and short-lived; they are called *free radicals,* or more simply, *radicals.*

This diatomic product, OH·, also violates our "normal" rules of valence. But we don't mind in this case, because this is simply the first step in an overall mechanism and not the balanced chemical reaction. We presume that this product will react further with other species to ultimately give the final product of the reaction. But what you can see is that we are allowed to step outside the regular rules for making compounds when dealing with mechanisms, because typically the intermediate chemical species aren't our final products anyway.

There are some basic guidelines, however. Since chemical species are interacting in three-dimensional space, we presume that individual elementary processes involve a single species, two species coming together (colliding), and *rarely* three species coming together. (Again, we emphasize "rarely": What are the odds that three different atoms or molecules will come to the exact point in three-dimensional space at the exact time in the necessary orientation so that a reaction will occur? It would be very rare. Elementary processes involving more than three species in the gas phase are not even seriously considered as possibilities.) Occasionally, collision with an inert reactant or the wall of the container can be invoked as part of an elementary process; such mechanisms are sometimes necessary to remove excess energy from two colliding reactants. But for the most part, elementary processes will involve one or two (maybe, but rarely, three) reactant species.

Also, the overall sum of all elementary processes must yield the balanced chemical reaction. This may seem obvious, but might be easily forgotten when proposing an overall mechanism.

Finally, the proposed mechanism must be consistent with the overall rate law of the reaction, which is determined experimentally. This point is important and useful. Earlier, we made the point that the exponents on the concentrations in the rate law, the orders with respect to each concentration, were not necessarily equal to the coefficient in the balanced chemical reaction. However, for elementary processes, the rate law *is* determined directly from the stoichiometry of the process. Instead of using the term "the order with respect to the reactants," we refer to "the *molecularity* with respect to the individual species" in the elementary process.

Example 20.10

What is the expected rate law of the equation below, assuming that it is an elementary process? What is the molecularity with respect to each reactant?

$$H_2 + O_2 \longrightarrow 2OH\cdot$$

Solution

According to the statement in the paragraph before the example, the rate law for this elementary process is given directly by the stoichiometry of the reaction. Therefore, we can simply look at the reaction (that is, we can tell "by inspection") and state that

$$\text{rate} = k[H_2]^1[O_2]^1$$

Since the exponent 1 is typically not written explicitly, the rate law is usually written as

$$\text{rate} = k[H_2][O_2]$$

The molecularity with respect to H_2 is 1, and the molecularity with respect to O_2 is also 1.

There is an additional consideration: is the rate law of this first elementary process consistent with the *experimentally determined* rate law of the overall reaction? Unfortunately, we don't know this yet, and the determination of this will be left to the next section. But you should at least be getting an idea of the factors involved in determining the mechanism of a reaction.

What are other possible elementary processes for this reaction? Below, we list some possible elementary processes. Note that the lack of charges on the species is intentional: many of the intermediates from the elementary processes are radicals.

$$H_2 + O_2 \longrightarrow 2OH\cdot \qquad \text{(from previously)}$$
$$OH\cdot + H_2 \longrightarrow H_2O + H\cdot$$
$$H\cdot + O_2 \longrightarrow OH\cdot + \cdot O\cdot$$
$$OH\cdot + H_2 \longrightarrow H_2O + H\cdot$$
$$H\cdot + \cdot O\cdot \longrightarrow OH\cdot$$
$$OH\cdot + H_2 \longrightarrow H_2O + H\cdot$$

and so on

The combination of all of these processes, for all of the billions of billions of molecules in any sample, is

$$2H_2 + O_2 \longrightarrow 2H_2O$$

As it should be.

Another example of elementary processes comes from halogenation of alkanes. For the gas-phase chlorination of methane, the major overall reaction (ignoring unwanted products) is

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

The individual steps in the mechanism are proposed to be

$$Cl_2 \longrightarrow 2\ Cl\cdot$$
$$Cl\cdot + CH_4 \longrightarrow HCl + CH_3\cdot$$
$$CH_3\cdot + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$$
$$Cl\cdot + CH_4 \longrightarrow HCl + CH_3\cdot$$
$$CH_3\cdot + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$$

and so on

Again, you can see that some of the products of each individual elementary process violate our normal rules of valence, but these are meant to be short-lived, intermediate chemical species. Some of the product species are free radicals, and others are the ultimate products of the reaction. Overall, the chemical reaction is

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

Again, as it should be.

Once a reaction has been broken down into its hypothetical individual steps, a normal question to ask is how fast these steps can go. Presumably, the overall reaction's rate will be dependent on the rates of the individual elementary processes. This is certainly the case, and modern chemical experimentation has actually gotten to the point that rates of certain elementary processes can be probed individually (for example, using ultrafast laser experiments). Knowing the rates of these individual steps is enormously helpful in understanding the rates of the net reaction.

There is a useful point, however: an overall reaction can go only as fast as its slowest step. The elementary process that has the slowest rate is the one that controls the rate of the overall chemical reaction. Steps before it get backed up, and steps after it go faster and deplete their reactants as fast as they are made. It's like a slow driver on a one-lane road. Cars behind the driver (like the steps before the slowest step) are backed up, and cars in front of that driver (like the steps after the slowest step) can speed away. It is the same idea with individual elementary processes. Because of this, the elementary process that controls the rate of the overall reaction is called the *rate-determining step* (or RDS for short).

In some cases, the RDS is the initial elementary process in a mechanism. If that's the case, then the rate law of the entire reaction is simple: it is just the rate law as dictated by the stoichiometry of the first elementary process. (Remember, although rate laws of overall reactions aren't necessarily related to the stoichiometry of the reaction, *they are for elementary processes.*) Suppose, for example, that the formation of water from H_2 and O_2 has an RDS that is the first elementary process in the mechanism. That process is

$$H_2 + O_2 \longrightarrow 2OH\cdot$$

In Example 20.10, we showed that the rate of this elementary process is given by

$$\text{rate} = k[H_2][O_2]$$

where k is some rate constant. However, if we can show that this step is the rate-*determining* step, then the rate for the *entire reaction* is

$$\text{rate} = k[H_2][O_2]$$

which is the same rate law.

At this point, we need to keep track of what process we are speaking of when we are referring to a rate. For elementary processes, the rate law can be determined directly from the stoichiometry of the process. For net balanced chemical reactions, we can't. However, we have proposed that we can know the rate of the overall reaction if we know the rate-determining step. We will see in the next section how we might be able to use the rate-determining step to relate to a measurable rate law.

(Counter?)Example 20.11

Assume that the rate law for the combination of hydrogen and oxygen is

$$\text{rate} = k[H_2][O_2]$$

Show that this is not consistent with the hypothesis that the second elementary process, which is

$$OH\cdot + H_2 \longrightarrow H_2O + H\cdot$$

is the rate-determining step in this reaction.

Solution

If the second elementary process in our proposed mechanism were the RDS, we could immediately predict a rate law of

$$\text{rate} = k[OH\cdot][H_2]$$

In this case, we have $[OH\cdot]$ substituting for $[O_2]$. Unless we can be convinced that the concentration of the hydroxide radical is equal to the concentration of diatomic oxygen, we would have a difficult time arguing that this rate law is equivalent to the assumed rate law from the first part of the example. This would argue against the second step being the RDS.

20.8 The Steady-State Approximation

The preceding example points out one obvious problem, and implies another. The obvious problem is that rate laws for elementary processes are not immediately transferable to rate laws for the overall reaction.

The implied problem is not so obvious. Typically, we determine rate laws in terms of amounts we can *measure.* For example, in the reaction between hydrogen and oxygen gases, we would want to express a rate law in terms of the amounts of H_2 and O_2. On the other hand, we certainly do *not* want to express a rate law in terms of, say, the OH radical. Such a chemical species may be an intermediate, but its existence is so fleeting that it would be extraordinarily difficult to measure its concentration at any one time, much less determine the effect its change in concentration has on a reaction rate. No, we typically express a rate law in terms of concentrations that are easily measured, like the concentrations of the reactants (and sometimes the products).

If the rate-determining step is the first step in the mechanism, then the rate law for the overall reaction is simply the rate law from the elementary process. (And because the first step does not have any intermediates as reactants, by definition the rate law can be expressed in terms of measurable quantities of chemical species.) Suppose, however, that the rate-determining step is the second step. Consider the following hypothetical two steps:

$$\mathrm{A} \longrightarrow \mathrm{B} \qquad \text{(fast)}$$

$$\mathrm{B} \longrightarrow \mathrm{C} \qquad \text{(slow)}$$

Here, B represents an intermediate product whose concentration is difficult to determine experimentally. A and C represent normal chemical reactants whose amounts can be measured. If the second step is the slow, rate-determining step, then it will force the first step to be backed up like cars on a one-lane road.

However, we do know that no chemical reaction actually ever goes to 100% completion. Rather, the reverse of the chemical reaction begins to occur and eventually an *equilibrium* is established. Since the first step is backed up by the second step, in many cases the reverse of the first step will begin to occur and eventually the first step will establish an equilibrium between its products and reactants. The two-step process is better represented as

$$\mathrm{A} \rightleftharpoons \mathrm{B} \qquad \text{(fast)}$$

$$\mathrm{B} \longrightarrow \mathrm{C} \qquad \text{(slow)}$$

where the $\rightleftharpoons$ arrows are used to symbolize an equilibrium. If this first step is truly in equilibrium, then the concentrations of A, B, and C are relatively steady and unchanging. Because of this, this model is called the *steady-state approximation* of reaction mechanisms.

The steady-state approximation helps us relate the rate law determined from the RDS with the rate law as determined from experiment. Recall that the rate law of a mechanism is dictated by the stoichiometry of the RDS, but how can we know if this rate law is consistent with the *experimental* rate law? We can use the fact that the preceding step(s) is/are at equilibrium to derive a rate law in terms of the original reactants (whose amounts or concentrations we can measure). There are two ways to do this. First, we will adopt a simplified approach. If the first step in the above two-step process is in fact in equilibrium, then we can write an equilibrium constant expression for it:

$$K = \frac{[\mathrm{B}]}{[\mathrm{A}]} \tag{20.59}$$

where we are using molar concentrations as an arbitrary unit of amount. (Thermodynamically, activities should be used, but using molarity still makes our point.) If the RDS is the second step, then we can immediately write a rate law for the reaction as

$$\text{rate} = k[\mathrm{B}]$$

But [B], the concentration of an intermediate species, may not be measurable! No matter. We will use equation 20.59 to find an expression for [B]:

$$K \cdot [\mathrm{A}] = [\mathrm{B}]$$

$$[\mathrm{B}] = K \cdot [\mathrm{A}]$$

If we substitute this expression for [B] into the rate law, we get

$$\text{rate} = \underbrace{k \cdot K}_{\text{constants}} \cdot [\mathrm{A}]$$

Since k and K are both constants, we will combine them into a *new* k' that is also some constant. The rate law becomes

$$\text{rate} = k' \cdot [\mathrm{A}]$$

which is a rate law in terms of A, a species whose concentration is knowable (as supposed a few paragraphs above).

Now: does this rate law agree with the experimentally determined rate law? If it does, then this mechanism—and the identification of the rate-determining step—is plausible. (Not proven, just plausible.) If this rate law does not agree with the experimentally determined rate law, then the mechanism is probably *incorrect.* By using approximations such as the steady-state one, we can try to judge whether a proposed mechanism is consistent with experimental observations.

In a more detailed approach, we recognize that the forward and reverse reactions in the equilibrium have their own characteristic rate constants and rate laws. For the reaction

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}$$

the forward reaction has the rate law

$$\text{rate} = k_1[\mathrm{A}]$$

The reverse reaction has the rate law

$$\text{rate} = k_{-1}[\mathrm{B}]$$

If we consider the fact that the intermediate B has a steady-state concentration, then its concentration is not changing over time. The way to write this using the tools of calculus is

$$\frac{d[\mathrm{B}]}{dt} = 0$$

The concentration of B increases due to the first step's forward reaction, but decreases due to the first step's reverse reaction as well as the rate-determining step's forward progress. Since the overall change in [B] is zero by the steady-state approximation, we can write (using k_2 for the rate constant of the second, rate-determining step)

$$\frac{d[\mathrm{B}]}{dt} = 0 = +\, k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] - k_2[\mathrm{B}] \tag{20.60}$$

(Recall that the RDS is $\mathrm{B} \xrightarrow{k_2} \mathrm{C}$, so the rate of disappearance of B from this process is simply $k_2[\mathrm{B}]$.) For a reaction whose rate-determining step gives us the rate law

$$\text{rate} = k_2[\mathrm{B}] \tag{20.61}$$

we can use equation 20.60 to substitute for the concentration of the intermediate B:

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]}{k_{-1} + k_2} = \frac{k_1}{k_{-1} + k_2} \cdot [\mathrm{A}] \tag{20.62}$$

Substituting for [B] in equation 20.61, we get for the rate law

$$\text{rate} = \underbrace{k_2 \cdot \frac{k_1}{k_{-1} + k_2}}_{\text{constant}} \cdot [\mathrm{A}]$$

Recognizing that the collection of constants equals some other constant, we again combine them into a constant k and write the above rate law as

$$\text{rate} = k \cdot [\mathrm{A}] \tag{20.63}$$

Notice that this is the same overall rate law that we got when we used the equilibrium constant of the first elementary process, so there is some consistency between the two mathematical applications of the steady-state approximation. The particular mathematical approach you might use depends on the information available (that is, the value of K or k_1 and k_{-1}) as well as what you might be trying to determine about a particular chemical reaction.

One kind of kinetics that uses the steady-state approximation is applied to enzyme-catalyzed reactions. Because enzymes (which are proteins) are very good catalysts, typically only a very small concentration is needed for a biochemical reaction to occur, and determination of the reaction kinetics focuses on following the change of concentration of the primary reactant, called the *substrate.*

The first step in an enzyme-catalyzed process is the combination of the proper enzyme, labeled E, with the substrate, labeled S. The second step, the RDS, is the production of some product material P and the simultaneous release of the unchanged enzyme catalyst. The two elementary steps are represented as

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES} \qquad \text{(fast)}$$

$$\mathrm{ES} \xrightarrow{k_2} \mathrm{E} + \mathrm{P} \qquad \text{(slow)}$$

where ES represents the intermediate, an enzyme-substrate complex. Because the second step is the RDS, the first elementary process reaches equilibrium, and we can apply the steady-state approach to the intermediate ES and derive, for the rate law,

$$\text{rate} = \frac{k_2 \cdot k_1}{k_{-1} + k_2} \cdot [\mathrm{E}][\mathrm{S}] = k[\mathrm{E}][\mathrm{S}] \tag{20.64}$$

where $k = k_2 \cdot k_1/(k_{-1} + k_2)$. Applying equation 20.62, the amount of enzyme-substrate complex ES is given by

$$[\mathrm{ES}] = \frac{k_1}{k_2 + k_{-1}}[\mathrm{E}][\mathrm{S}] \tag{20.65}$$

We define $[\mathrm{E}_0]$ as the total amount of enzyme present in any form:

$$[\mathrm{E}_0] \equiv [\mathrm{E}] + [\mathrm{ES}] \tag{20.66}$$

Using equation 20.65, we can rewrite the expression for $[\mathrm{E}_0]$ as

$$[\mathrm{E}_0] = [\mathrm{E}] + \frac{k_1}{k_2 + k_{-1}}[\mathrm{E}][\mathrm{S}] = [\mathrm{E}]\left(1 + \frac{k_1}{k_2 + k_{-1}}[\mathrm{S}]\right)$$

Solving for [E], we find that

$$[\mathrm{E}] = \frac{[\mathrm{E}_0]}{1 + \dfrac{k_1}{k_2 + k_{-1}}[\mathrm{S}]} = \frac{[\mathrm{E}_0](k_2 + k_{-1})}{k_2 + k_{-1} + k_1[\mathrm{S}]}$$

In terms of $[\mathrm{E}_0]$, the rate of the equation is

$$\begin{aligned}\text{rate} &= \frac{k_2 \cdot k_1}{k_{-1} + k_2} \cdot [\mathrm{E}][\mathrm{S}] \\ &= \frac{k_2 \cdot k_1 \cdot [\mathrm{E}_0]}{k_2 + k_{-1} + k_1[\mathrm{S}]} \cdot [\mathrm{S}]\end{aligned}$$

By defining V and K as

$$V \equiv k_2[\mathrm{E}_0] \quad \text{and} \quad K \equiv \frac{k_{-1} + k_2}{k_1} \tag{20.67}$$

we can write the *reciprocal* of the rate, 1/rate, as

$$\frac{1}{\text{rate}} = \frac{1}{V} + \frac{K}{k_2[\mathrm{E}_0]} \cdot \frac{1}{[\mathrm{S}]} \tag{20.68}$$

A plot of 1/rate versus 1/[S], the inverse of the substrate concentration, gives a straight line with slope $K/(k_2[\mathrm{E}_0])$ and y-intercept $1/V$. Equation 20.68 is called the *Michaelis-Menten equation,* and a plot of 1/rate versus 1/[S] is called a *Lineweaver-Burk plot.* An example of such a plot is shown in Figure 20.18. This is one common application of the steady-state approximation to enzyme kinetics.

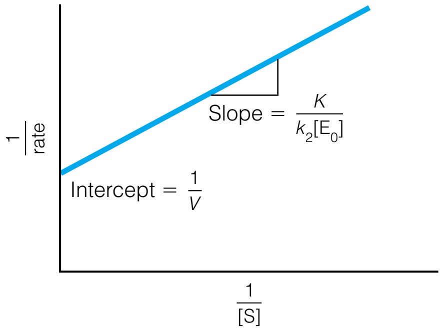

Figure 20.18 A Lineweaver-Burk plot of a reaction that follows the Michaelis-Menten equation. A graph of 1/rate versus 1/[S] should give a straight line with slope $K/(k_2[\mathrm{E}_0])$ and intercept $1/V$.

20.9 Chain and Oscillating Reactions

The kinetics of certain kinds of reactions are interesting enough that they deserve special attention. In this section, we will consider two interesting kinds of reaction kinetics.

Consider a gas-phase reaction in which one or two reactant species are converted into species that are very reactive themselves. For example, a molecule of bromine can be broken into two individual bromine atoms, each with an unpaired electron:

$$\mathrm{Br{-}Br} \longrightarrow \mathrm{Br\cdot} + \mathrm{Br\cdot} \tag{a}$$

In turn, each of these bromine atoms, which are free radicals, can react with another species, say a hydrogen molecule:

$$\mathrm{Br\cdot} + \mathrm{H_2} \longrightarrow \mathrm{H{-}Br} + \mathrm{H\cdot} \tag{b}$$

A new free radical, in this case a hydrogen atom with an unpaired electron, is generated. This reactive free radical can now react with an unreacted bromine molecule to make a product molecule and another free radical:

$$\mathrm{H\cdot} + \mathrm{Br_2} \longrightarrow \mathrm{H{-}Br} + \mathrm{Br\cdot} \tag{c}$$

The newly generated bromine atom, a free radical, can react with another hydrogen molecule as shown in reaction b, after which the new hydrogen atom can react with another bromine molecule as given in reaction c, and so forth. Such a reaction cycle can continue undiminished until one reactant is virtually depleted, or until two free radicals combine to make a molecule that is relatively unreactive, like each of these:

$$\begin{aligned} \mathrm{Br\cdot} + \mathrm{Br\cdot} &\longrightarrow \mathrm{Br{-}Br} \\ \mathrm{Br\cdot} + \mathrm{H\cdot} &\longrightarrow \mathrm{H{-}Br} \\ \mathrm{H\cdot} + \mathrm{H\cdot} &\longrightarrow \mathrm{H{-}H} \end{aligned} \tag{d}$$

This series of kinetic steps typifies a chain reaction. A *chain reaction* is a reaction whose mechanism consists of steps whose products are intermediates that react to form other intermediates, usually in an apparently cyclical fashion. Reaction a, which started the chain reaction in this example, is called an *initiation reaction* (or initiation step). Reactions b and c of this example react one intermediate and produce another intermediate. They are called *propagation* *reactions.* The reactions d represent a loss of the intermediates that propagate the chain reaction. They are called *termination steps.* All steps can be generally characterized by the change in the reactive intermediates over the course of the reaction. Initiation steps form reactive intermediates from reactants, propagation steps react an intermediate but form another (so there is no net change in the amount of reactive intermediate), and termination steps decrease the number of reactive intermediates. A reaction does not have to involve free radicals to be a chain reaction, although free-radical reactions are the most common examples of chemical chain reactions.

Many polymerization processes proceed via free-radical mechanisms. Also, the Cl-atom-catalyzed reactions that contribute to stratospheric ozone depletion are free-radical reactions that have received a lot of attention in recent years.

Example 20.12

In the discussion of rate-determining steps in section 20.7, the chlorination of methane, CH_4, was postulated to occur by a free-radical mechanism:

$$Cl_2 \longrightarrow 2Cl\cdot \tag{a}$$

$$Cl\cdot + CH_4 \longrightarrow HCl + CH_3\cdot \tag{b}$$

$$CH_3\cdot + Cl_2 \longrightarrow CH_3Cl + Cl\cdot \tag{c}$$

$$Cl\cdot + CH_4 \longrightarrow HCl + CH_3\cdot \tag{d}$$

$$CH_3\cdot + Cl_2 \longrightarrow CH_3Cl + Cl\cdot \tag{e}$$

a. Classify each reaction a–e as initiation or propagation.
b. No termination step is given above. Suggest some possible termination steps for this reaction.

Solution

a. Since the first reaction creates two free radicals where none existed as reactant, reaction a is an initiation reaction. All other reactions have a reactive intermediate (a free radical) as a reactant and as a product, so reactions b through e are propagation reactions.
b. A termination reaction reduces the number of reactive intermediates. In this example, a termination reaction would have two radicals combining to make a stable molecule. There are three possibilities:

$$Cl\cdot + Cl\cdot \longrightarrow Cl_2$$

$$Cl\cdot + CH_3\cdot \longrightarrow CH_3Cl$$

$$CH_3\cdot + CH_3\cdot \longrightarrow CH_3CH_3$$

Experimentally, the presence of a small amount of ethane, CH_3CH_3, is seen as support of the chain reaction mechanism for this chemical reaction.

Although all reactions proceed with some change in energy, initiation and termination reactions usually have an obvious energy change. For initiation reactions, there is typically some energy input to promote the formation of reactive intermediates. In other words, many initiation reactions are endothermic. Or, the initiation reaction might occur spontaneously from the molecules from the higher-energy end of the energy distribution (remember from kinetic theory that there is a range of energies for molecules at any given temperature). More formally, an initiation reaction should indicate this energy input, which can be in the form of heat, light, or some other process:

$$\text{reactants} \xrightarrow{\text{energy}} \text{intermediates} \qquad \text{(initiation)}$$

For termination reactions, the formation of a stable product implies that energy is released (that is, it is an exothermic process). The energy given off must go somewhere. Typically, the energy is either given off as photons or, more commonly, a third body is needed to absorb the energy given off as the reactive intermediates react to form a stable product. If the third body is given the symbol M, then a termination reaction between two free radicals R· can be written as

$$\text{R}\cdot + \text{R}\cdot + \text{M} \longrightarrow \text{R–R} + \text{M}^* \qquad \text{(termination)}$$

where M* is an energetically excited third body. Third bodies can be reactant or product molecules, some other species like an inert gas (an example of *homogeneous termination*), or even the walls of the container defining the system (an example of *heterogeneous termination*).

Under some conditions, intermediate reactions that actually generate more reactive intermediates can contribute significantly to the propagation of the reaction. These reactions are more properly called *branching reactions.* One example, from the mechanism of the reaction between H_2 and O_2 gases, is

$$\text{H}\cdot + \text{O}_2 \longrightarrow \text{HO}\cdot + \cdot\text{O}\cdot \qquad \text{(branching)}$$

In this example, the reaction goes from having one reactive free radical to two reactive free radicals. These two reactive products can participate in their own propagation reactions, like

$$\text{HO}\cdot + \text{H}_2 \longrightarrow \text{H}_2\text{O} + \text{H}\cdot$$

$$\text{O} + \text{HO}\cdot \longrightarrow \text{O}_2 + \text{H}\cdot$$

or other steps. Branching reactions contribute to an increase in the number of propagation reactions, and if more branching reactions occur, more and more propagation reactions will occur as a result. Under the right conditions, branching reactions can contribute to a geometric increase in the number of propagation processes that occur (that is, 2 → 4 → 8 → 16 → 32 → · · · as shown in Figure 20.19). Since most propagation reactions are exothermic, a geometric increase in the number of propagation reactions is accompanied by a geometric increase in the amount of energy released. The result is an *explosion.*

Not all explosions are caused by branching reactions, and not all chain reaction mechanisms lead to explosions. But a branching chain reaction is one cause for a gas-phase explosion, under the right conditions. If there are enough inert bodies or the area of the walls of the container is large enough with respect to the volume, enough termination reactions can occur to minimize the effect of branching reactions, and no explosion occurs. If the concentrations of the reactants are not in the right proportions, not enough branching reactions will occur to cause a geometric increase in the energy given off by the overall reaction, and no explosion occurs. As an example, the H_2/O_2 system has been studied extensively, and the relative partial pressures, temperatures, and other variables have been mapped to determines conditions under which explosions

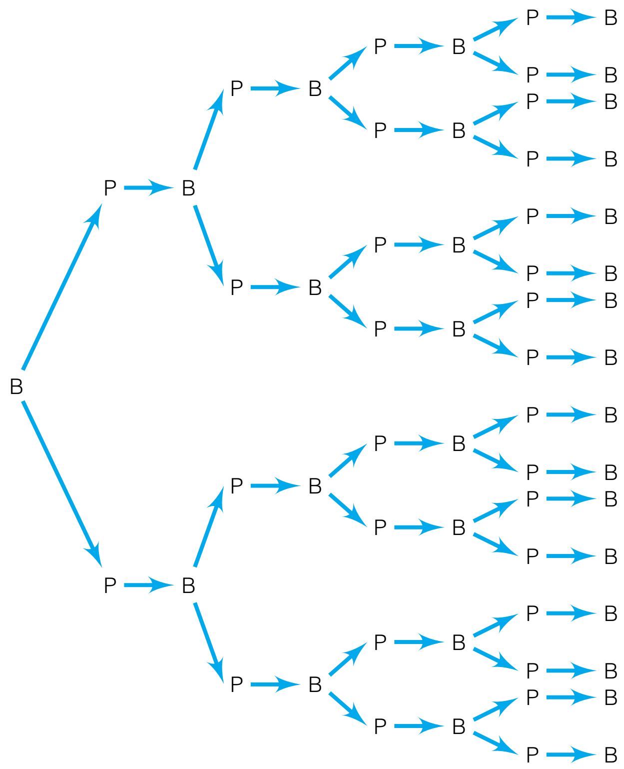

Figure 20.19 Branching reactions increase the number of propagation reactions, which can lead to an explosion. In the figure, P stands for a propagation and B represents a branching reaction.

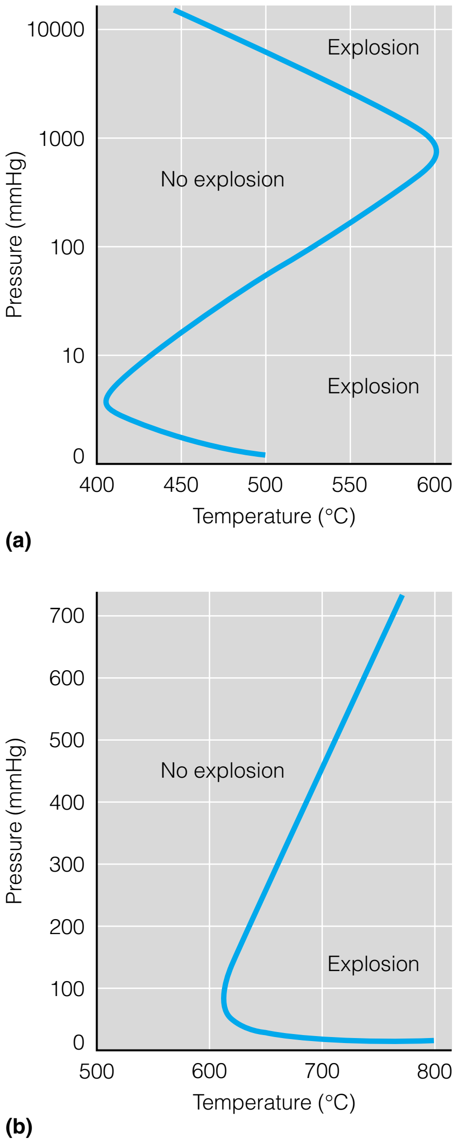

Figure 20.20 Graphs of explosion limits for gaseous mixtures. (a) Stoichiometric mixtures of H_2 and O_2. (b) Stoichiometric mixtures of CO and O_2.

will occur. Figure 20.20 shows a diagram of some of those conditions for H_2/O_2 mixtures.

Another example of interesting kinetics is the *oscillating reaction.* In these reactions, an apparent oscillation in a concentration of an intermediate is seen during the course of the reaction. This concentration oscillation can be seen as a color-change cycle, the periodic formation of a gaseous product, or some other measurable increase-and-decrease in the concentration of some species. Oscillating reactions are rare but are particularly fascinating to chemists because of their seemingly unusual behavior.

Oscillating reactions might seem to violate the laws of thermodynamics, which suggest that a reaction should proceed toward equilibrium and, once there, not deviate from equilibrium conditions unless some external influence is imposed. Oscillating reactions start from some nonequilibrium condition, appear to pass through some equilibrium concentration of products, then continue to a different nonequilibrium concentration. At some point, the reaction reverses and proceeds back toward the equilibrium amounts, again passing through the equilibrium condition to some other extreme, then reverses again. The analogy is a clock pendulum swinging back and forth, but the general understanding of chemical reactions is that they should proceed toward equilibrium and then stop, a dynamic equilibrium having been established.

One key in understanding oscillating reactions is that the oscillating concentration is typically one of an intermediate, which may or may not be a final product of the overall reaction. Another key is the idea that there are two (or more) pathways that the reaction can take, and that the intermediate is a product of one pathway and a reactant of another. Thus, when the intermediate's concentration is low, the intermediate-producing pathway is favored; and when the intermediate's concentration is high, the intermediate-consuming pathway is favored. Eventually, the reaction comes to equilibrium as final products are formed (ultimately in accordance with thermodynamics).

In 1910–1920, the American biophysicist Alfred Lotka* proposed two simple mechanisms for oscillating reactions. Using hypothetical reactants and products, the two mechanisms are as follows:

$$\begin{aligned} \mathrm{A} &\longrightarrow \mathrm{B} \\ \mathrm{B + C} &\longrightarrow \mathrm{2C} \qquad \text{(mechanism 1)} \\ \mathrm{C} &\longrightarrow \mathrm{D} \end{aligned}$$

$$\begin{aligned} \mathrm{A + B} &\longrightarrow \mathrm{2B} \\ \mathrm{B + C} &\longrightarrow \mathrm{2C} \qquad \text{(mechanism 2)} \\ \mathrm{C} &\longrightarrow \mathrm{D} \end{aligned}$$

In both cases, the overall reaction is simply A → D, with B and C as intermediate species. Each individual step in a mechanism has a rate law based on the stoichiometry of the individual elementary process. Lotka showed that if [A] is assumed to be constant (that is, it is present in a large excess), the differential equations that relate the concentrations of A, B, C, and D have mathematical solutions that predict oscillations in the concentrations of intermediates B and C if the rate constants have the appropriate values. In mechanism 1, [B] and [C] follow damped oscillations, and for mechanism 2 the intermediate concentrations oscillate more evenly. Figure 20.21 shows the concentration behaviors of the intermediates versus time.

At the time of Lotka's work, no chemical reaction was known to follow his two mechanisms. In 1921, W. C. Bray reported an oscillation in a liquid-phase reaction between hydrogen peroxide and potassium iodate ($H_2O_2 + KIO_3$), but this report was treated with some skepticism. In 1951, the Russian biophysicist Boris Belousov discovered another example of an oscillating reaction, which was studied in detail by his fellow Russian biophysicist Anatol M. Zhabotinsky. Despite initial resistance to the thought of oscillating reactions (Belousov's initial work wasn't published until 1959, and Zhabotinsky's detailed studies weren't done until the mid 1960s), the *Belousov-Zhabotinsky* (or BZ) *reaction* is now the best-known example of an oscillating chemical reaction.

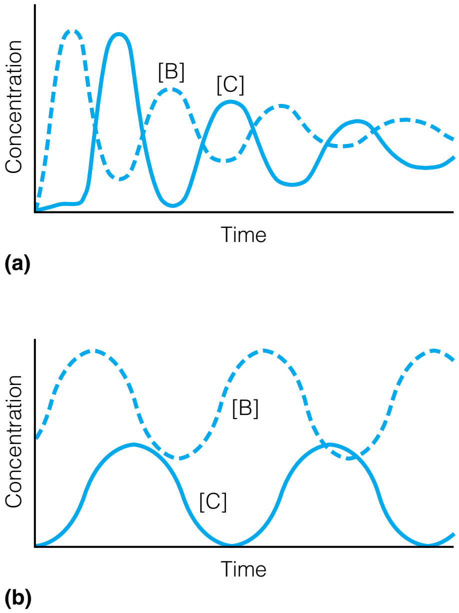

Figure 20.21 (a) In Lotka's first mechanism for an oscillating reaction, the concentrations of intermediates B and C oscillate in a damped fashion (that is, the oscillations get less and less extreme). (b) In Lotka's second mechanism, the concentrations of the intermediates oscillate in a more regular fashion—at least in the short term.

The reaction is actually a group of reactions that have some common ingredients. Generally, a BZ reaction is the metal-ion-catalyzed oxidation of certain carboxylic acids by bromate (BrO_3^-) ions. A common catalyst is the cerium(IV) ion, Ce^{4+}. One example of an overall reaction is

$$\mathrm{2HBrO_3\ (aq) + 3\ malonic\ acid} \xrightarrow{\mathrm{Ce^{4+}}} \mathrm{2\ bromomalonic\ acid + 4H_2O + 3CO_2\ (g)} \qquad \mathbf{(20.69)}$$

The steps in the mechanism of the BZ reaction are complex (an 18-step mechanism has been proposed!), but the two pathways can be summarized as

$$\begin{aligned} \mathrm{BrO_3^- + Br^-} &\longrightarrow \mathrm{HBrO_2 + Br^-} \longrightarrow \text{products} \qquad \text{(path I)} \\ \mathrm{BrO_3^- + HBrO_2} &\longrightarrow \mathrm{HBrO_2} \longrightarrow \mathrm{Br^-} + \text{products} \qquad \text{(path II)} \end{aligned}$$

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*Lotka's models have also been applied to the understanding of animal populations in ecology. Although animals aren't molecules, the "kinetics" of their populations follows similar differential equations!

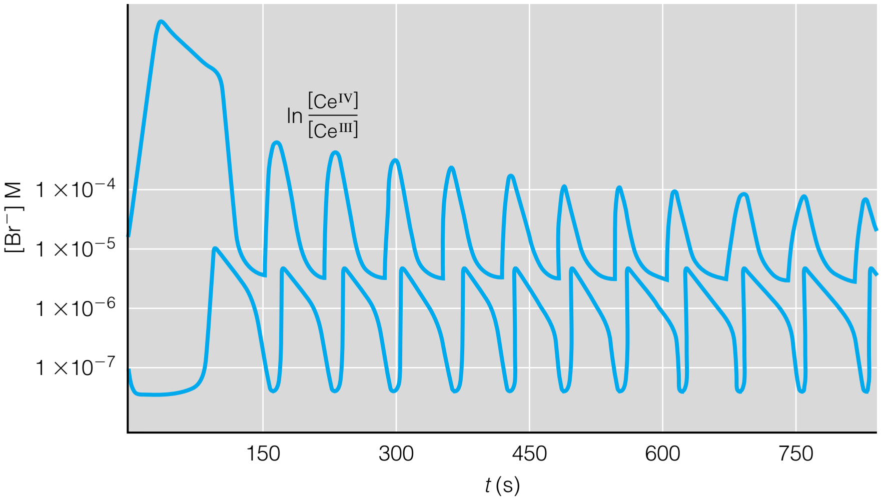

Figure 20.22 The oscillating nature of the Belousov-Zhabotinsky reaction can be illustrated by the varying concentrations of some of the species involved. Many of these concentrations are measured electrochemically. *Source:* Reprinted with permission from the *Journal of the American Chemical Society,* Vol. 94, No. 25, p. 8651.


Richard Magna/Fundamental Photographs

Figure 20.23 Under certain conditions, oscillating reactions can produce different colors over time, leading to some fascinating visual displays.

Both pathways react bromate ion to products, but path I has Br^- ions as a reactant whereas path II has Br^- ions as a product. Thus, when enough Br^- is available, path I dominates; when $[Br^-]$ is small, path II is favored. Path II then generates Br^- ions, so as $[Br^-]$ increases, path I becomes favored, . . . and the cycle goes on. Ce^{4+} is reduced to Ce^{3+} by some steps in path II, then reoxidized to Ce^{4+} by other steps in the same pathway. As such, the reaction serves as a Ce(III)/Ce(IV) half-reaction, and the oscillations can be followed electrochemically by using the BZ reaction itself as a half cell. Various indicators and spectroscopic techniques can also be used to follow the changing concentrations of the intermediates. Figures 20.22 and 20.23 show diagrams of how concentrations change during the course of a BZ reaction.

Why are chemists interested in oscillating reactions? Not only are they interesting from a kinetic perspective, but some important chemical reactions are oscillatory in nature. Among the most important ones are the reactions that cause a heart to beat. Specific chemical processes promote electrochemical responses that cause the heart to contract, pump blood—and keep us alive. An understanding of oscillating reactions thus yields a better understanding of the biochemistry of complex living systems.

20.10 Transition-State Theory

Not all kinetics is phenomenological. In recent years there have been advances in understanding the kinetics of reactions from a theoretical perspective. In this section, we will review the basics of some theoretical kinetics.

Collision theory is a simple description of reacting molecules that treats them as hard spheres. Some of the basic concepts of collision theory were considered at the end of section 20.6. Although this model does predict some numerical reaction parameters having about the right order of magnitude, its description of molecules as hard spheres and use of steric factors as "fudge factors" ignores the complex nature of even simple molecular reactions. A more realistic approach is necessary.

Transition-state theory (sometimes called *activated-complex theory*) is a more realistic model of a bimolecular elementary step in a reaction. It takes

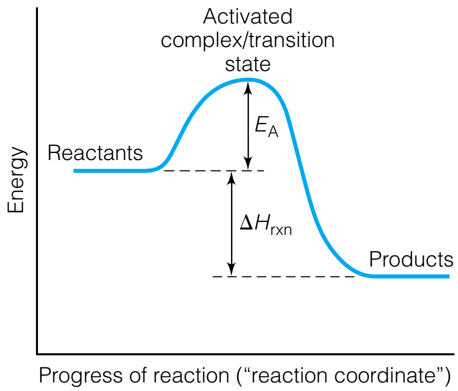

Figure 20.24 A reaction profile is a diagram illustrating the relationship between the energy of the reactants, the energy of the products, and the energy of the proposed intermediate species called the activated complex or the transition state. The difference between the energies of the reactants and the transition state is Arrhenius's proposed activation energy.

into account the molecular orientations that are thought necessary to promote a reaction (and so take into account what collision theory calls the steric factor) as well as the energy barrier that reactants must overcome to become products (taking into account what collision theory calls the activation energy). Two new concepts are needed to understand transition-state theory. The *reaction coordinate* is the conceptual pathway taken as the two reactant molecules become products. Plots of total energy of the bimolecular system versus the reaction coordinate are called *reaction profiles,* illustrated in Figure 20.24. The maximum on the reaction profile curve represents the potential energy barrier the reactants must overcome to react. The *transition state* (or *activated complex*) is the intermediate structure of the two molecules that exists at the potential energy maximum.[†]

A key point in transition-state theory is to calculate a theoretical rate constant k for the bimolecular elementary process. In terms of transition-state theory, the bimolecular elementary process given as

$$\mathrm{A} + \mathrm{B} \longrightarrow \text{products}$$

can be further broken down into two steps involving the transition state C*:

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} \mathrm{C}^* \qquad \textbf{(a)}$$

$$\mathrm{C}^* \xrightarrow{k^*} \text{products} \qquad \textbf{(b)}$$

where k and k^* represent the rate constants of the two imaginary steps, k for the bimolecular step a and k^* for the unimolecular step b. If the reaction considered is in fact an elementary process, then from the ideas in section 20.7, the rate laws can be written in terms of the stoichiometry of the reaction:

$$\text{rate} = k[\mathrm{A}][\mathrm{B}] = k^*[\mathrm{C}^*] \qquad \textbf{(20.70)}$$

The second equality in equation 20.70 is a basic assumption that species A and B become some transition state C* on their way to forming products, so the rate of the elementary process can be expressed in terms of the concentrations of original reactants *or* in terms of the amount of the transition state. We can rewrite equation 20.70 in terms of the elementary process rate constant k as

$$k = \frac{k^*[\mathrm{C}^*]}{[\mathrm{A}][\mathrm{B}]} \qquad \textbf{(20.71)}$$

The concentrations in equation 20.71 correspond to a concentration-based equilibrium constant of the first reaction in the hypothetical two-step process, so we define a dimensionless K_c^* as

$$\frac{K_c^*}{c^\circ} = \frac{[\mathrm{C}^*]}{[\mathrm{A}][\mathrm{B}]} \qquad \textbf{(20.72)}$$

where c° represents the standard concentration unit (that is, 1 M or $a = 1$) to make the expression unitless. We rewrite the expression for k, equation 20.71, as

$$k = \frac{K_c^* \cdot k^*}{c^\circ}$$

[†] Although many references use the terms *transition state* and *activated complex* interchangeably, other references define them differently. For example, some references refer to the point on the reaction profile as the transition state, and to the molecular species at that point as the activated complex itself. We will not worry about such subtleties here.

Thus, if we can determine K_c^* and k^*, we can calculate the rate of the elementary process.

The rate constant k^* for the second step of our hypothetical two-step process is relatively easy to express. Consider how a transition state rearranges to a set of product species: typically, one chemical bond of the transition state will lengthen as two parts of the transition state separate into the ultimate products. The lengthening of a chemical bond is part of a molecular motion known as a *vibration,* just like the vibrations considered for stable molecules in Chapters 12 and 14. Therefore, we assume that the transition state has some vibrational frequency ν^* that "connects" the transition state and the ultimate products. (Like any polyatomic species, a transition state has other vibrations, but only one particular vibration represents the movement from the transition state to the products.) Understanding that a unimolecular rate constant like k^* has units of s^{-1} (that is, seconds in the denominator), we submit that the rate constant k^* should be proportional to the transition state's vibrational frequency ν^* (also units of s^{-1}) that promotes the formation of products. The variable κ, called the *transmission coefficient,* is defined as the proportionality constant, yielding

$$k^* = \kappa \cdot \nu^* \tag{20.73}$$

as our expression for the unimolecular rate constant for step b. Transmission coefficients are usually assumed to be 1, and k^* is simply equal to ν^*.

We turn our attention to K_c^* by applying some results from Chapter 18: we can use statistical thermodynamics to determine a numerical value for the equilibrium constant K_c^*. For the reaction

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} \mathrm{C}^*$$

the equilibrium constant expression in terms of the partition functions of A, B, and C* is

$$K_c^* = \frac{q_{\mathrm{C}^*}/V}{(q_\mathrm{A}/V)(q_\mathrm{B}/V)} \tag{20.74}$$

(see equation 18.62). Each individual partition function can be separated into five parts: translational, electronic, vibrational, rotational, and nuclear. Let us consider two of these parts. First, using equation 18.8, the electronic parts of the partition function can be written as

$$\frac{q_{\mathrm{el,C}^*}}{q_{\mathrm{el,A}} \cdot q_{\mathrm{el,B}}} = \frac{(e^{D_\mathrm{e}/kT})_{\mathrm{C}^*}}{(e^{D_\mathrm{e}/kT})_\mathrm{A} \cdot (e^{D_\mathrm{e}/kT})_\mathrm{B}} = \frac{(e^{D_\mathrm{e}/kT})_{\mathrm{C}^*}}{e^{(D_\mathrm{e,A}+D_\mathrm{e,B})/kT}} \tag{20.75}$$

where the D_e's in the exponentials refer to the dissociation energies of the respective species. The difference between D_e of C* and $(D_\mathrm{e,A} + D_\mathrm{e,B})$ is simply the difference in the electronic energies of C* and species (A and B), collectively. We will use $-\Delta\epsilon^*$ to represent the difference in the electronic energies; a negative sign is used by convention and * means that it refers in part to the transition state. Equation 20.75 becomes

$$\frac{q_{\mathrm{el,C}^*}}{q_{\mathrm{el,A}} \cdot q_{\mathrm{el,B}}} = e^{-\Delta\epsilon^*/kT} \tag{20.76}$$

If we use q' to represent the remaining partition functions within each q, equation 20.74 becomes

$$K_{c^*} = \frac{q'_{\mathrm{C}^*}/V}{(q'_\mathrm{A}/V)(q'_\mathrm{B}/V)} \cdot e^{-\Delta\epsilon^*/kT}$$

We also consider the vibrational partition function of C*. It has $3N - 6$ (or $3N - 5$) terms in it, but one of those terms represents the vibration that tracks the movement of C* into products. The high-temperature-limit partition function for this term is (from equation 18.20)

$$q_{\nu^*} = \frac{kT}{h\nu^*}$$

Let us remove this one term from the overall partition function for C* and represent the leftover partition function (minus this one vibrational term and the electronic term) as q''. We have, for $K_c{}^*$:

$$K_c{}^* = \frac{q''_{C^*}/V}{(q'_A/V)(q'_B/V)} \cdot e^{-\Delta\epsilon^*/kT} \cdot \frac{kT}{h\nu^*} \tag{20.77}$$

Combining this expression with the expression for the rate constant k^*, equation 20.73, we can get an expression for the rate constant k for the bimolecular reaction:

$$k = \frac{\kappa \cdot \nu^*}{c^\circ} \cdot \frac{q''_{C^*}/V}{(q'_A/V)(q'_B/V)} \cdot e^{-\Delta\epsilon^*/kT} \cdot \frac{kT}{h\nu^*}$$

The ν^* terms cancel and, if κ is presumed to be 1, we get

$$k = \frac{kT}{c^\circ h} \cdot \frac{q''_{C^*}/V}{(q'_A/V)(q'_B/V)} \cdot e^{-\Delta\epsilon^*/kT} \tag{20.78}$$

This last equation is one form of the *Eyring equation,*[†] and is used to estimate k for a bimolecular elementary process. (Careful about the two uses of the variable k in the above equation!) For a given set of reactants A and B and a stated temperature, all of the quantities in equation 20.78 can be calculated *for a given structure of a transition state* C*. Therefore, if you had a known or proposed transition state, you would be able to calculate $\Delta\epsilon^*$ and q for the transition state C*, and for given reactants A and B you should certainly be able to determine the partition functions (since they are typically known, stable molecules). All other parameters are fundamental constants, so the rate constant k can be calculated.

Note the parallel between equation 20.78 and the Arrhenius equation

$$k = A \cdot e^{-E_A/RT}$$

According to transition-state theory, the pre-exponential factor A is given by the expression

$$A = \frac{kT}{c^\circ h} \cdot \frac{q''_{C^*}/V}{(q'_A/V)(q'_B/V)} \tag{20.79}$$

Thus, we have an opportunity to calculate A from theoretical perspectives and compare it to experimentally determined values (as determined, for example, by graphing ln k versus $1/T$). Table 20.2 lists some simple reactions and their experimental and calculated pre-exponential factors. Agreements are typically about the correct order of magnitude.

Because of the relationship between an equilibrium constant and the Gibbs free energy, we can use K^* to define a ΔG^* value for the formation of the tran-

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[†] It is named after Henry Eyring, a twentieth-century chemist who did some fundamental work in kinetics, including enunciation of the steady-state theory.

Table 20.2 Experimental and calculated pre-exponential factors

	$A[\text{cm}^3/(\text{mol}\cdot\text{s})]$	
Reaction	**Experimental**	**Calculated**
$H + H_2 \longrightarrow H_2 + H$	5.4×10^{13}	7.4×10^{13}
$H_2 + Br \longrightarrow HBr + H$	3×10^{13}	1×10^{14}
$H + CH_4 \longrightarrow H_2 + CH_3$	1×10^{13}	2×10^{13}
$CH_3 + H_2 \longrightarrow CH_4 + H$	2×10^{12}	1×10^{12}
$ClO + ClO \longrightarrow Cl_2 + O_2$	6×10^{10}	1×10^{11}

Source: J. Nicholas, *Chemical Kinetics: A Modern Survey of Gas Reactions,* Wiley, New York, 1976.

sition state, and rewrite the Eyring equation in terms of the Gibbs free energy. We get

$$k = \frac{kT}{c^\circ h} \cdot e^{-\Delta G^*/RT} \tag{20.80}$$

where k on the left is the rate constant, whereas k on the right is Boltzmann's constant. Since ΔG can be written in terms of ΔH and ΔS, we can rewrite equation 20.80 as

$$k = \frac{kT}{c^\circ h} \cdot e^{-\Delta H/RT} \cdot e^{\Delta S^*/R} \tag{20.81}$$

where now we are referring to an enthalpy change for the formation of the transition state, ΔH^*, and an entropy change for the formation of the transition state, ΔS^*. Equation 20.81 is similar to the Arrhenius equation, but not exactly. However, if we write the logarithm of the Arrhenius equation as

$$\ln k = \ln A - \frac{E_A}{RT}$$

we differentiate with respect to temperature:

$$\frac{\partial \ln k}{\partial T} = \frac{\partial \ln A}{\partial T} - \frac{\partial}{\partial T}\left(\frac{E_A}{RT}\right)$$

The term $(\partial \ln A)/\partial T$ is zero (A is a constant, so the derivative is zero), and we can evaluate the derivative of the activation energy. We get

$$\frac{\partial \ln k}{\partial T} = \left(\frac{E_A}{RT^2}\right)$$

We can rearrange this to

$$E_A = RT^2 \frac{\partial \ln k}{\partial T} = RT^2 \frac{1}{k}\frac{\partial k}{\partial T} \tag{20.82}$$

We can substitute the expression for k from equation 20.81 into equation 20.82 to find that

$$E_A = \Delta H^* + 2RT \quad \text{or} \quad \Delta H^* = E_A - 2RT \tag{20.83}$$

In terms of the activation energy, k can be written as

$$\begin{aligned} k &= \frac{kT}{c^\circ h} \cdot e^{-(E_A - 2RT)/RT} \cdot e^{\Delta S^*/R} \\ &= \frac{kT}{c^\circ h} \cdot e^{-E_A/RT} \cdot e^{-(-2RT)/RT} \cdot e^{\Delta S^*/R} \end{aligned}$$

which can be rearranged to

$$k = \frac{e^2 kT}{c^\circ h} \cdot e^{-E_A/RT} \cdot e^{\Delta S^*/R} \qquad \textbf{(20.84)}$$

Equating the activation-energy exponentials in equation 20.84 and the Arrhenius equation, the rest of the terms in equation 20.81 must be related to the pre-exponential factor. Thus, using an experimentally known pre-exponential factor, we can estimate the entropy change that accompanies the formation of the transition state using the equation

$$A = \frac{e^2 kT}{c^\circ h} \cdot e^{\Delta S^*/R} \qquad \textbf{(20.85)}$$

Thus, we do find some connections between kinetics and thermodynamics after all.

Example 20.13

For the two-step process

$$\mathrm{H} + \mathrm{H_2} \longrightarrow \mathrm{H_3} \longrightarrow \mathrm{H_2} + \mathrm{H}$$

H_3 is the transition state for this hydrogen transfer reaction. If the pre-exponential factor were found to be 5.4×10^7 $\mathrm{m^3/(mol{\cdot}s)}$ at 25.0°C, predict the value of ΔS^*. Comment on its sign and magnitude. Use a standard concentration of 1 M = 1 mol/L = (1000 mol)/$\mathrm{m^3}$.

Solution

The pre-exponential factor has been expressed in standard units, but as always we should be careful about the units we use. Using equation 20.85, we have

$$5.4 \times 10^7 \frac{\mathrm{m^3}}{\mathrm{mol{\cdot}s}} = \frac{e^2 kT}{c^\circ h} \cdot e^{\Delta S^*/R}$$

All the fundamental constants have known values, so substituting:

$$5.4 \times 10^7 \frac{\mathrm{m^3}}{\mathrm{mol{\cdot}s}} = \frac{e^2(1.381 \times 10^{-23}\ \mathrm{J/K})(298\ \mathrm{K})(\mathrm{m^3})}{1000\ \mathrm{mol}(6.626 \times 10^{-34}\ \mathrm{J{\cdot}s})} \cdot \exp\left[\frac{\Delta S^*}{8.314\ \mathrm{J/(mol{\cdot}K)}}\right]$$

We get, with initial canceling of the joule and kelvin units on the right side:

$$5.4 \times 10^7 \frac{\mathrm{m^3}}{\mathrm{mol{\cdot}s}} = 4.589 \times 10^{10} \frac{\mathrm{m^3}}{\mathrm{mol{\cdot}s}} \cdot \exp\left[\frac{\Delta S^*}{8.314\ \mathrm{J/(mol{\cdot}K)}}\right]$$

The units $\mathrm{m^3/(mol{\cdot}s)}$ appear on both sides, so they cancel. Rearranging:

$$1.2 \times 10^{-3} = \exp\left[\frac{\Delta S^*}{8.314\ \mathrm{J/(mol{\cdot}K)}}\right]$$

Taking the natural logarithm of both sides and solving:

$$-6.75 = \frac{\Delta S^*}{8.314\ \mathrm{J/(mol{\cdot}K)}}$$

$$\Delta S^* = -56.1 \frac{\mathrm{J}}{\mathrm{mol{\cdot}K}}$$

A comment on the result: a decrease in entropy suggests a transition state that is more organized than the reactants. When you consider that this reaction is forming a single triatomic complex from two individual species, it makes sense that the entropy decreases.

20.11 Summary

Exactly how a chemical reaction proceeds may have very little to do with the balanced chemical equation. Kinetics is the study of exactly how a reaction proceeds. Kinetics usually focuses on how the rate of a chemical reaction varies with the concentration of the individual reactants, and tries to determine a simple mathematical model, a rate law, that describes how fast a reaction will proceed. Kinetics can also relate the rate of a reaction with the absolute temperatures, using the Arrhenius equation or modifications of this equation. Also, the more intimate details of a chemical reaction are given by the elementary processes of a chemical reaction. The combination of all of the elementary processes, called the mechanism of a reaction, shows us exactly how a chemical reaction does indeed proceed. Understanding how a reaction proceeds gives us enormous insight into how chemicals react and gives us handles on how we might be able to control that reaction. Finally, we are able to apply some basic theoretical ideas to elementary processes and, using our knowledge of statistical thermodynamics, estimate the rate constants of simple reactions.

20.2 Rates and Rate Laws

20.1. Write three additional rate relationships like equation 20.5 using the definition of the rates from equations 20.3 or 20.4.

20.2. The oxidation-reduction reaction between iron metal and aqueous permanganate ions in acidic solution is

$$16H^+ (aq) + 5Fe (s) + 2MnO_4^- (aq) \longrightarrow 2Mn^{+2} (aq) + 5Fe^{2+} + 4H_2O (\ell)$$

At some temperature, the reaction proceeds at such a rate that 1.00 millimole of H^+ is consumed in 2 minutes 33.8 seconds. What is the (invariant) rate of this reaction in units of moles per second?

20.3. The oxidation-reduction reaction between iron metal and aqueous permanganate ions in acidic solution is

$$16H^+ (aq) + 5Fe (s) + 2MnO_4^- (aq) \longrightarrow 2Mn^{+2} (aq) + 5Fe^{2+} + 4H_2O (\ell)$$

At some temperature, the reaction proceeds at such a rate that 1.00 millimole of H^+ is consumed in 2 minutes 33.8 seconds. What is the rate of this reaction in units of moles of each reactant per second and moles of each product per second? How do these answers differ from the answer in the previous problem?

20.4. Consider the chemical reaction

$$A + B + C \longrightarrow \text{products}$$

Determine the order with respect to A, B, and C, and construct the complete rate law (including the value of the rate law constant) from the following experimental data.

Initial rate (M/s)	[A]	[B]	[C]
6.76×10^{-6}	0.550	0.200	1.15
9.82×10^{-7}	0.210	0.200	1.15
1.68×10^{-6}	0.210	0.333	1.15
9.84×10^{-7}	0.210	0.200	1.77

20.5. Explain how a species might be part of a rate law but not part of a balanced chemical reaction.

20.6. Refer to Example 20.2 and explain whether any useful information can be obtained by comparing the first and the third set of data.

20.7. Rate law experiments don't always give data in the form of a rate in moles per second. Some of them give an amount of time necessary for a reaction to proceed to a given point. The faster the rate, the less time necessary. For the following data, assume that the time given is to react 0.10 M of A. Determine the complete rate law for the reaction $A + B \rightarrow$ products.

Time taken (s)	[A]	[B]
36.8	0.20	0.40
25.0	0.20	0.60
10.0	0.50	0.60

(A classic chemical reaction/demonstration called the *iodine clock reaction* is usually measured this way.)

20.8. A researcher determined the rate law

$$\text{rate} = k \cdot [A]^2$$

for a simple chemical reaction. If the rate was 2.44×10^{-4} M/s when [A] was 0.167 M, what would [A] be when the rate of the reaction is 1.55×10^{-6} M/s?

20.9. What must the units on k be for the following rate law?

$$\text{rate} = k \cdot [A]^2[B]^2$$

20.3 Characteristics of Rate Laws

20.10. Derive equation 20.15.

20.11. Explain why plotting $[A]_t$ versus time, as equation 20.15 might suggest, would *not* yield a straight-line plot for a first-order reaction.

20.12. To a very good approximation, the cooling of a hot body to room temperature follows first-order kinetics. (In this case, however, the unit that is changing is kelvins, not molarity. This idea is known as Newton's law of cooling.) If the rate constant for a body is $0.0344\ s^{-1}$, how long would it take for a piece of matter to go from 1000 K to 298 K?

20.13. Assume that thermal decomposition of mercuric oxide, HgO, follows first-order kinetics. It can be followed by the production of oxygen gas as a product:

$$2HgO (s) \longrightarrow 2Hg (\ell) + O_2 (g)$$

At a particular temperature, $k = 6.02 \times 10^{-4}\ s^{-1}$. If 1.00 gram of HgO were present initially, how long would it take to produce **(a)** 1.00 mL of O_2 (g) at STP; **(b)** 10.0 mL of O_2 (g) at STP? (STP = standard temperature and pressure for a gas.)

20.14. Assume that thermal decomposition of mercuric oxide, HgO, follows second-order kinetics with the same numerical value given in exercise 20.13 for k (but different units). Answer **(a)** and **(b)** above under that assumption. Compare the answers with the ones from above.

20.15. Derive equation 20.20 from equation 20.19.

20.16. Derive equation 20.22.

20.17. **(a)** Write a rate law and an integrated rate law for a chemical reaction that follows third-order kinetics in one of the reactants. **(b)** What would you have to plot on a graph in order to get a straight line for a reaction that follows third-order kinetics?

20.18. Derive an expression for the half-life of **(a)** a third-order reaction; **(b)** a reaction whose order is −1; **(c)** a reaction whose order is $\frac{1}{2}$. (In these last two cases, examples are rare but known.)

20.19. What are the slope and y-intercept of a straight line plotted for a zeroth-order reaction?

20.20. Rewrite equation 20.27 so that it has the form of a straight-line equation and identify the expected slope(s) and intercept(s) of two possible plots.

20.21. Use equation 20.24 to determine the time it takes for a zeroth-order reaction to come to completion.

20.22. When ionic compounds crystallize from a supersaturated solution, the crystallization front (that is, the barrier between the crystalline solid and the supersaturated solution) typically travels at a constant speed through the solution until it reaches the boundaries of the system, then stops. What order of rate law is described by this behavior?

20.23. An aqueous reaction that uses the solvent H_2O as a reactant has a given rate law of

$$\text{rate} = k \cdot [H_2O][A]$$

where A is the other reactant species. Explain why, in most circumstances, this reaction can be defined in terms of pseudo first-order kinetics. What are the units on the rate constant?

20.24. If a reaction has the same rate constant, what time does it take for a reactant to decrease by 5% (that is, still near the beginning of the reaction process) if the kinetics are zeroth-order, first-order, and second-order with respect to that reactant?

20.25. List at least four experimentally determined parameters that you, an experimenter, can define when exploring the hydrolysis of ethyl benzoate by aqueous sodium hydroxide.

20.26. Will a plot of the base-10 logarithm of the concentration, log $[A]_t$, versus time give a straight-line plot for a first-order reaction? If so, what does the slope of this line equal?

20.4 & 20.5 Equilibrium, Parallel, and Consecutive Reactions

20.27. Explain why a zeroth-order reaction probably won't be zeroth-order for two complete half-lives.

20.28. For the reaction $A + B \rightleftharpoons C + D$, various initial rate measurements were run using A and B only, and C and D only. From the data below, calculate the equilibrium constant for the reaction.

Rate (M/s)	[A]	[B]
1.081×10^{-5}	0.660	1.23
6.577×10^{-5}	4.01	1.23
6.568×10^{-5}	4.01	2.25

Rate (M/s)	[C]	[D]
7.805×10^{-7}	2.88	0.995
1.290×10^{-6}	2.88	1.65
1.300×10^{-6}	1.01	1.65

20.29. Show how equation 20.33 reduces to a simpler form of an integrated first-order rate law when the reverse reaction of an equilibrium is negligible.

20.30. Write expressions like equation 20.37 for a set of three parallel reactions from the same reactant. Use k_1, k_2, and k_3 for the three rate constants.

20.31. A trisaccharide is a carbohydrate that is composed of three sugar ("saccharide") molecules. Consider a trisaccharide composed of three different sugars and represented by A-B-C. In acidic solution, the carbohydrate will hydrolyze in two possible ways:

$$\text{A–B–C} \xrightarrow{k_1} \text{A} + \text{B–C}$$

$$\text{A–B–C} \xrightarrow{k_2} \text{A–B} + \text{C}$$

If $k_1 = 4.40 \times 10^{-5}\ s^{-1}$ and $k_2 = 3.95 \times 10^{-4}\ s^{-1}$, what is the ratio A–B/B–C initially? Can you determine the ratio A–B/B–C when the reaction reaches equilibrium?

20.32. Show that the set of three equations 20.44 satisfies the law of conservation of matter for the stoichiometry of the general chemical reaction that is used. (*Hint:* consider that the initial amount of material is given by $[A]_0$, and show that at equilibrium the amount of material is still $[A]_0$.)

20.33. For a simple set of two parallel reactions, the decrease of the initial species A is easy to follow graphically by taking the logarithm of equation 20.38. What is the slope of this straight-line graph? Is there an easy way to determine the individual values from this plot alone?

20.34. Can one determine the forms of straight-line graphs for equations 20.41 and 20.42, keeping in mind that time, *t*, is usually the variable that is plotted on the ordinate (that is, the *x*-axis)? Why or why not?

20.35. Consider the answers to the two previous questions. *Now* can the two individual rate constants k_1 and k_2 be determined? How would that be done?

20.36. In Example 20.7, we showed that there will be a "momentary" buildup of the intermediate product, ^{210}Po.

(a) Use the $[B]_t$ expression in equation 20.47 to derive an expression for the time it takes for the *maximum* amount of ^{210}Po to be present. Here's what to do: take the derivative of the expression for $[B]_t$ with respect to time, set it equal to zero (since if the amount is at a maximum, the plot of the amount versus time has a slope of zero), and solve for time *t*.

(b) Use this value for time and equations 20.47 to determine the specific amounts of ^{210}Bi, ^{210}Po, and ^{206}Pb when the amount of ^{210} Po is at a maximum.

20.37. For what values of time, *t*, will ^{210}Bi and ^{206}Pb be at a maximum? (See exercise 20.36.)

20.38. An interesting pair of consecutive reactions involve the absorption of ethyl alcohol by the body, which is a first-order process, and the consequent oxidation of alcohol to acetaldehyde by liver alcohol dehydrogenase (LADH), which is a zeroth-order process. The differential changes in the three states of ethanol can therefore be described as

$$-\frac{d[A]}{dt} = k_1[A]_t$$

$$\frac{d[B]}{dt} = k_1[A]_t - k_2$$

$$\frac{d[C]}{dt} = k_2$$

which are slightly modified from equations 20.46. The integrated form of the first equation is the same as for two consecutive first-order reactions, but for the second and third reactions, they will not be.

(a) What do A, B, and C stand for in this example?

(b) Determine an integrated form for [B] over time. Do this by finding an integrated expression for $[A]_t$ (*Hint:* refer to the chapter!), substitute for $[A]_t$ in the second expression, rearrange the infinitesimals, and integrate one side over [B] as the variable and the other side over time, *t*, as the variable. The integrations are actually simpler than for the consecutive first-order reaction example in the chapter itself.

(c) Determine an integrated form for [C] over time.

(d) Rough values of k_1 and k_2 for people are $3.00 \times 10^{-3}\ s^{-1}$ and 4.44×10^{-5} mol/s, respectively. Use your expressions for the amounts over time to plot a graph of $[A]_t$, $[B]_t$, and $[C]_t$ versus time. (A graphing calculator or a computer with a graphing program would be useful.) Use 1.00 mol of C_2H_5OH as $[A]_0$. Vary this value and see how it affects the graphs of $[A]_t$, $[B]_t$, and $[C]_t$.

20.39. Find limiting forms of equations 20.47 for **(a)** $k_1 \gg k_2$, and **(b)** $k_1 \ll k_2$.

20.6 Temperature Dependence

20.40. Express equation 20.48 as if it were referring to a graph. What is being plotted, and what does the expression $-(\Delta_{rxn}H)/R$ represent?

20.41. Nitrous oxide, N_2O, can be decomposed thermally. The following values for the rate constant *k* were determined (S. K. Ross et al., *J. Phys. Chem. A,* 1997, 101: 1104) at the following temperatures:

k [cm³/(molecule·second)]	*T* (K)
6.79×10^{-16}	2056
8.38×10^{-16}	2095
1.03×10^{-15}	2132
1.39×10^{-15}	2173

Does this reaction follow the Arrhenius equation? What is the estimated pre-exponential factor?

20.42. Derive equation 20.54 from equation 20.53. Beware of the 1/*T* part of the denominator in the derivative.

20.43. One rule of thumb has been that a chemical reaction doubles in speed for every 10° increase in absolute temperature from room temperature (nominally 295 K). If this is strictly true, what is the activation energy of the chemical reaction?

20.44. At room temperature (22°C), the rate constant for proton transfer between water molecules in solution is about $1 \times 10^{11}\ s^{-1}$, which is one of the fastest known reactions. If the activation energy for this process equals one-half of the O–H bond strength of 498 kJ/mol, what is the pre-exponential factor *A* for this reaction?

20.45. Recently, researchers studying the kinetics of metal atom reactions with small gas molecules measured a rate constant for the gas-phase reaction of

$$Co + NO \longrightarrow \text{products}$$

as $9.9 \times 10^{-12}\ cm^3/s$ at 1153 K. If the activation energy of this reaction is 1.9 kJ/mol, what is the value of the pre-exponential factor?

20.46. A reaction has $k = 1.77 \times 10^{-6}$ 1/(M·s) at 25.0°C and an activation energy of 20.0 kJ/mol. **(a)** What order is the reaction? **(b)** What is the value of the rate constant at 100°C?

20.47. A reaction has $k = 1.77 \times 10^{-6}$ 1/(M·s) at 25.0°C and an activation energy of 20.0 kJ/mol. What is the value of the rate constant at 100° C? Compare this answer to the answer in part b of the previous exercise and comment on the effect of the activation energy on rate law constants.

20.48. Scientists use very focused "molecular beams" of gas-phase atoms and molecules in high-vacuum systems to study one-step chemical processes. For the gas-phase molecular beam reaction between sodium atoms and methyl chloride to make sodium chloride and the methyl radical,

$$Na + CH_3Cl \longrightarrow NaCl + CH_3\cdot$$

the probability of the reaction depends on the orientation of the methyl chloride molecule with respect to the sodium atom. Suggest a possible interaction geometry that would account for this result. Why would the probability for reaction *not* depend on the orientation of the other reactant?

20.49. Chemical processes that are triggered by photons are also understood using the kinetics concepts mentioned in this chapter. The chemistry of vision is one example. The currently accepted mechanism for vision involves a compound called rhodopsin, which is composed of a protein molecule (opsin) attached to a colored polyene molecule called *cis*-retinal. (*Cis*-retinal is chemically related to a class of molecules called carotenes, which are highly colored compounds responsible for the colors of carrots and tomatoes. Eating carrots does help vision, specifically in low light.) The vision process begins when the *cis*-retinal absorbs a photon and is isomerized about one of its double bonds to make *trans*-retinal:

$$cis\text{-retinal} \xrightarrow{h\nu} trans\text{-retinal}$$

The reaction is energetically favorable; the photon's energy is apparently necessary only to overcome an activation energy barrier.

(a) The least energetic photon that is considered visible light has a wavelength of 750 nm. What is the activation energy for the isomerization reaction?

(b) If the rate constant at 37°C is $3 \times 10^{11}\ s^{-1}$, what is the pre-exponential factor *A* for this reaction?

(c) The Antarctic icefish lives in Southern Hemisphere waters that can reach −2°C. Assuming that this chemical process is the same in an icefish eye, what is *k* at this temperature?

20.50. Nitric oxide, NO, is known to break down ozone, O_3, by the following bimolecular reaction:

$$NO\ (g) + O_3\ (g) \longrightarrow NO_2\ (g) + O_2\ (g)$$

If the activation energy of this reaction is 10.5 kJ/mol and the pre-exponential factor is 7.9×10^{11} cm³/(mol·s), **(a)** what is the rate constant of this reaction at 298 K? **(b)** If the ozone concentration were 5.4×10^{-12} mol/cm³ and the NO concentration were 2.0×10^{-12} mol/cm³ (conditions that might exist in a high-pollution area), what is the rate of this reaction?

20.7 & 20.8 Mechanisms and Steady States

20.51. (a) Suggest a mechanism for the bromination of ethane:

$$Br_2 + CH_3CH_3 \longrightarrow CH_3CH_2Br + HBr$$

(b) Would you expect that this reaction might go faster or slower than the chlorination of methane? (*Hint:* consider the strengths of the bonds involved in the initial steps of the mechanism.)

20.52. Derive equation 20.62.

20.53. Explain why a "consecutive reaction" analysis would not be appropriate for a mechanism in which the second step is the RDS. That is, why can't we write that mechanism in terms of A → B → C in this case?

20.54. Determine a rate law for the chlorination of methane assuming that the first step is the rate-determining step.

20.55. Determine a rate law for the chlorination of methane assuming that the second step is the rate-determining step and that the first step can be approximated by the steady-state approximation. What is the difference between the answer here and the answer for the previous exercise?

20.56. A proposed mechanism for the gas-phase chlorination of methane is

$$Cl_2 + CH_4 \longrightarrow CH_4Cl + Cl\cdot$$

$$CH_4Cl \longrightarrow CH_3\cdot + HCl$$

$$CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$$

$$Cl\cdot + CH_4 \longrightarrow CH_3\cdot + HCl$$

and so on

Suppose the first step is the RDS. What is the expected rate law in terms of the original reactants, Cl_2 and CH_4? How would you determine if this mechanism might be a potentially correct (or, for that matter, a potentially incorrect) one?

20.57. Consider the proposed mechanism in the previous problem. Now assume that the second step is the RDS. Use the steady-state approximation to determine a rate law in terms of the original reactants. *Now* how would you determine if this mechanism might be correct?

20.58. Many gas-phase reactions require some inert body, usually represented as M, to absorb or supply energy in a collision in order to proceed. In the spontaneous decomposition of ozone, O_3, we can suggest the mechanism

$$O_3 + M \longrightarrow O_3{}^* + M$$

$$O_3{}^* \xrightarrow{\text{RDS}} O_2 + \cdot O\cdot$$

$$\cdot O\cdot + O_3 \longrightarrow 2O_2$$

for the overall reaction

$$2O_3 \longrightarrow 3O_2$$

In the mechanism, $O_3{}^*$ refers to an ozone molecule in some energetically excited state that can react spontaneously to form O_2 and O atoms. Determine the rate law of the proposed mechanism in terms of O_3 and M, where the second step is the rate-determining step. Will adding an inert gas like Ar to a sample of ozone increase or decrease the rate of the reaction?

20.59. Show that equation 20.68 is equivalent to equation 20.64.

20.60. Carbonic anhydase, an enzyme whose substrate is CO_2, has a K of 12 mM. When the concentration of CO_2 is 1.4×10^{-4} M, the rate of reaction between carbonic anhydrase and CO_2 is 2.72×10^{-7} mol/s, and when the concentration of CO_2 is 2.2×10^{-4} M, the rate is 4.03×10^{-7} mol/s. If the reaction follows Michaelis-Menten kinetics, what is V for this reaction?

20.61. Show that another form of the Michaelis-Menten equation is

$$\text{rate} = \frac{V[S]}{K + [S]}$$

20.62. When $[S] = K$, what is the value of the rate of a reaction that follows Michaelis-Menten kinetics? Considering the answer, what use do you think this might be?

20.9 Chain and Oscillating Reactions

20.63. Most halogenation reactions of hydrocarbons proceed via a free-radical chain reaction mechanism. Of the halogens Cl_2, Br_2, and I_2, which initiation reaction should proceed most easily? Explain your answer.

20.64. The free-radical reaction $H_2 + I\cdot \rightarrow HI + H\cdot$ has a pre-exponential factor of $2.4 \times 10^{11}\ M^{-1 \cdot s^{-1}}$ and an activation energy of 142 kJ/mol. Predict its rate constant at 400 K.

20.65. Pyrolysis involves heating compounds to break them into smaller molecules, and typically involves free-radical chain reactions. Pyrolysis of crude oil fractions is a common method of making smaller hydrocarbons from large-chain hydrocarbons. Pyrolysis of ethane, C_2H_6, forms ethylene and hydrogen gases (C_2H_4 and H_2) as the primary products. Suggest a mechanism for this pyrolysis reaction, labeling your reactions as initiation, propagation, and termination steps.

20.66. Nuclear fission reactions can also proceed by chain reaction. Consider an ideal nuclear fission reaction as

$${}^{235}U + {}^{1}n \longrightarrow {}^{92}Kr + {}^{141}Ba + 2\,{}^{1}n$$

Suggest conditions under which this reaction does not proceed; conditions under which this reaction maintains a chain reaction; and conditions under which significant branching occurs (leading to an explosion).

20.67. Label the elementary processes for the reaction between H_2 and O_2 (see section 20.7) as initiation, propagation, branching, or termination reactions.

20.68. Write the rate laws for elementary processes for the proposed mechanisms 1 and 2 of oscillating reactions.

20.69. What are the rate laws of mechanisms 1 and 2 for oscillating reactions if the second reactions were the rate-determining steps?

20.10 Transition-State Theory

20.70. Estimate ΔG^* for an elementary process whose rate constant k is $8.5 \times 10^{-1}\ M^{-1}\cdot s^{-1}$ at 450 K.

20.71. For the following two reactions

$$H + Cl_2 \longrightarrow HCl + Cl$$

$$H + Br_2 \longrightarrow HBr + Br$$

the first reaction has a lower value of *A* than the second reaction. What can one say about the relative properties of the intermediates HCl_2 and HBr_2, just from the relative values of *A*?

20.72. For the reaction

$$NaI + Cl \longrightarrow NaCl + I$$

propose a structure for the transition state and list what data are needed to determine a value of *k* using transition-state theory.

20.73. Explain how (or if) equation 20.84 is consistent with the general statements of the laws of thermodynamics that reactions tend toward lower energy and higher entropy.

20.74. If all other factors are the same, a change in ΔS^* from +1 J/(mol·K) to −1 J/(mol·K) leads to what percentage change in the rate constant *k*?

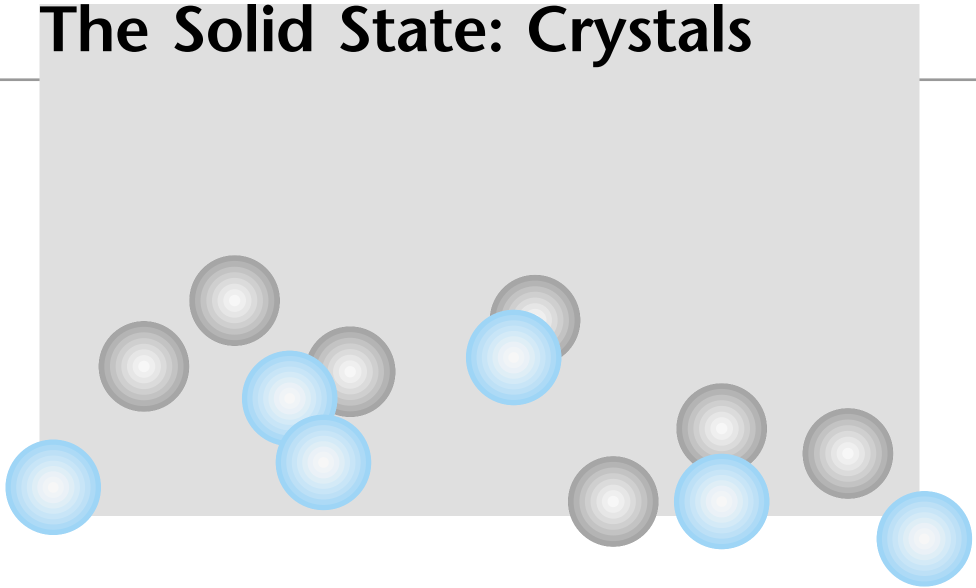
Symbolic Math Exercises

20.75. Consider a reaction that has two parallel pathways (both first-order) to products. Pathway 1, leading to product B, has a rate constant of $1.34 \times 10^{-5}\ s^{-1}$. Product C–producing pathway 2 has a rate constant of $6.55 \times 10^{-4}\ s^{-1}$. Plot the concentrations of A, B, and C versus time, and determine the time necessary to produce the maximum amount of the kinetically favored product.

20.76. Consider a set of first-order consecutive reactions $A \rightarrow B \rightarrow C$. The rate constants are $8.4 \times 10^{-4}\ s^{-1}$ and $3.02 \times 10^{-5}\ s^{-1}$, respectively. Plot the concentrations of A, B, and C versus time, and determine the time necessary to produce the maximum amount of the intermediate product B.

21

The Solid State: Crystals



IT'S A CURIOUS THING that elementary physical chemistry can describe a molecule-based model of the gas phase (from the various gas laws to the kinetic theory of gases) and the solid phase, but not the liquid phase. At one extreme, the behavior of gas particles is so independent and random that we can model their behaviors statistically. At the other extreme, the crystalline solid, the individual particles (whether atoms, ions, or molecules) are distributed so regularly that it takes little knowledge to be able to describe the entire solid. The liquid phase has neither advantage, so its description is not so simple and is considered beyond the scope of this book. (In some respects, this is unfortunate, since many processes that are most important to us—like the biological processes of life itself—occur in the liquid phase.)

Because of the regularity in a well-ordered solid, we can describe its structure, properties, and behaviors mathematically. That connects the study of the solid phase to physical chemistry: we can model our understanding of the solid state. That's what physical chemistry does: provide models for understanding matter. Since much of matter is in (or can be in) the solid state, a model for understanding the solid phase is useful, just as having a model for the gas phase is useful. This chapter introduces some of the concepts used to understand the solid phase.

21.1 Synopsis

First, we will consider the general types of solids. Many solids do not exist as a random arrangement of atoms and molecules. Some do, but we will focus on those solids that exist as some regular arrangement of atoms or molecules. We will find that there are only a few possible ways for regular arrangements, called crystals, to exist. First, we will describe those ways. It turns out that the regularity of crystals can be described by a very small arrangement of atoms and molecules; this very small arrangement, repeated many times in three dimensions, can tell us a lot about the properties of the solid.

How do we determine these regular arrangements? As with spectroscopy, we can use electromagnetic radiation as a probe. But rather than absorbing or emitting radiation, crystalline solids can diffract radiation under certain conditions. These conditions are dictated by the structure of the crystal, and there is a simple rule for relating the diffraction effect to the crystal's structure.

We will also find that the type of crystal a certain compound makes is not necessarily arbitrary, that there is a recognizable energy of interaction between the components of certain crystals, that crystals are not perfect, and that society actually takes advantage of such imperfections in a big way.

21.2 Types of Solids

Before we can discuss the solid phase, we need to define several different types of solid phases. The individual particles (atoms, ions, or molecules) that make up a solid can exist either in random arrangements in three-dimensional space or in an ordered, repeating arrangement. Randomly arranged solids are called *amorphous* ("without shape") or *glassy.* As you might expect, glass is one example of a solid that is usually amorphous; see Figure 21.1. Many polymers have no large-scale order and so can also be considered amorphous.

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Figure 21.1 Amorphous or glassy materials, like the ones shown, have randomly arranged molecules. Crystalline materials, on the other hand, are solids that are built up of units that repeat in three dimensions.

Solids that are arranged in an orderly fashion are called *crystalline.* Most solids form large, well-formed crystals if they are prepared carefully enough—solidified from the liquid or gas phase very slowly, for example. (Even large biomolecules like hormones, proteins, and DNA can form crystals. For example, the hormone insulin was first crystallized by the American biochemist John J. Abel in 1925.) If not prepared carefully, many solids form a host of tiny crystals and would be described as *polycrystalline.*

Crystalline solids are further categorized by type of crystal. Covalently bonded molecules can form *molecular crystals,* which are regular three-dimensional arrangements of the individual molecules. One good example is water, H_2O: as a molecular compound, the individual molecules of water have some regular arrangement in a crystal of H_2O. Any covalent compound (like the large biomolecules mentioned earlier) forms molecular crystals, easily or with difficulty, given the chance. Molecular crystals are relatively soft and have low melting points. Figure 21.2 shows an example of one molecular crystal.

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Figure 21.2 Molecules can form crystals, if they are positioned regularly in three dimensions.

Compounds that are composed of ions form *ionic crystals.* In this case, the need for opposite charges—cations and anions—to neutralize each other dictates a certain arrangement of ions in a crystal. Ionic crystals are typically very hard but very brittle (that is, they break easily if subjected to sudden forces). They also tend to have relatively high melting points. Coulombic attractions between opposite charges is the strongest known force; it takes a lot of energy, in the form of temperature, to break those attractions and turn an ionic solid into a liquid.

A few solids make an almost infinite three-dimensional array of covalent bonds to neighboring atoms. Such solids are called *covalent network solids.* Diamond (a form of carbon), elemental silicon, elemental germanium, and silicon dioxide are examples (see Figure 21.3). Although few solids can be described this way, the ones that can have distinctive properties: they are very hard with high melting points. It takes a lot of energy, either mechanical or thermal, to break the almost infinite network of covalent bonds.

Finally, certain elements are hard but ductile and malleable, conduct electricity, are shiny, and have variable but usually high melting points. These elements are metals, and their collective characteristics are explained by an idea called *metal bonding.* In this type of bonding, the electrons of the individual metal atoms "pool" together to become electrons not of the individual atoms but of the whole solid. This explains the electrical conductivity of metals, and

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Figure 21.3 Some covalently bonded materials, like silicon dioxide, form crystals that are (practically) infinite, regular arrays of atoms in a covalent network.

deeper analysis of this idea explains their other characteristics, too. This is beyond our scope, but understand that the interactions between atoms of metals is a different sort of crystalline bonding that does in fact account for the unique properties of metals.

In this chapter, we focus on crystalline solids. Although there are techniques for studying the structure of amorphous solids, they will not be considered here.

21.3 Crystals and Unit Cells

Solids that have some regular, three-dimensional order are examples of *crystals.* A crystal is any solid that has a repetitious structure. The repetition can be of molecules (forming a molecular crystal), ions, or atoms. One can always find the smallest group of molecules, ions, or atoms that when repeated in three dimensions reproduces the entire crystal. This smallest group is called the *unit cell* of the crystal.

Unit cells themselves are three-dimensional, but it helps to first envision them in two dimensions. Figure 21.4 shows a two-dimensional array of black and white dots making a "crystal." The box shows a unit cell. Notice that the way the unit cell is marked, it includes only part of each white dot at each corner and the entire black dot in the center. This is the correct way to draw the unit cell. Imagine, now, that this cell is copied, moved to the lower right, and placed adjacent to the original unit cell. Imagine also that the copy is moved to the upper right and placed adjacent to the original unit cell. Figure 21.5 shows these extensions of the unit cell. By placing these unit cells adjacent to each other over and over again, the complete two-dimensional crystal can be reproduced.

Why can't the unit cell in Figures 21.4 and 21.5 simply consist of two white dots and two black dots? Because that arrangement ignores the space between the dots. The correct unit cell must be able to reproduce the entire crystal, which includes not just the positions of the particles but the space in between them.

Nor is the unit cell drawn in Figure 21.4 and 21.5 the only possible unit cell. Figure 21.6 shows a few other possibilities. Which is the correct unit cell? Convention requires that the unit cell be the *smallest* part of the crystal that can reproduce the entire crystal. Therefore, the unit cells depicted in Figure

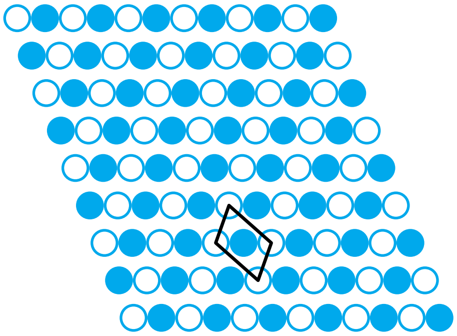


Figure 21.4 A unit cell is the smallest part of a crystal that when repeated in all directions reproduces the complete crystal. Here, the unit cell has a dark atom in the center and takes a quadrant out of the four white corner atoms.

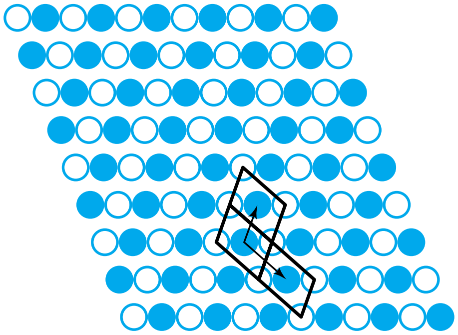


Figure 21.5 Translating the unit cell to adjacent positions starts to map out the complete crystal. Although this diagram shows translations to only two adjacent positions, additional translations eventually allow us to map out the entire two-dimensional crystal. Real unit cells do the same thing, but in three dimensions.

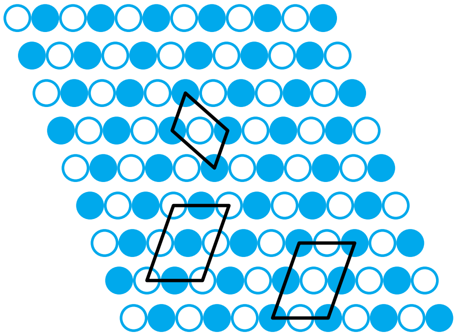


Figure 21.6 Other possible unit cells. However, convention requires that the smallest reproducible part of the crystal be considered the true unit cell. The top unit cell is a true unit cell (compare this to the unit cell in Figure 21.4!); the bottom two cells are not.

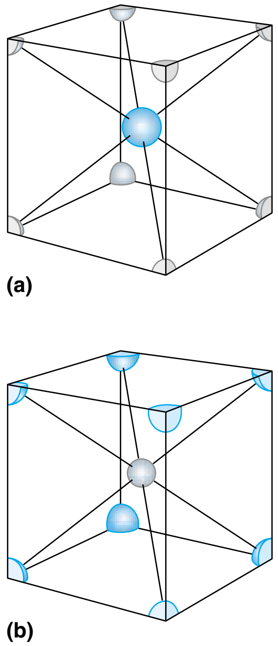


Figure 21.7 Two possible unit cells for CsCl. Either can be considered a correct unit cell.

21.4 and the top of Figure 21.6 are considered the unit cells; the two lower cells in Figure 21.6 are not considered proper unit cells.

Figure 21.7 shows two possible unit cells for a very simple ionic crystal, CsCl. Again, note that the corners of the unit cell contain only part of the atom at that corner. In Figure 21.7a, each corner contains $\frac{1}{8}$ of a cesium atom. Collectively, the eight corners of the unit cell give $8 \times \frac{1}{8} = 1$ Cs atom per cell, and a single chlorine atom is in the center of the cell. This gives us a 1 : 1 ratio of Cs atoms to Cl atoms in the compound, agreeing with the ratio of atoms in the formula unit CsCl. In Figure 21.7b, the chlorine atoms are at the corners, but inspection of the unit cell shows that this unit cell also supports CsCl as the formula unit for this compound.

Figure 21.7 illustrates an important point in the determination of the unit cell: the same species is typically found at the corners—and, as we will see shortly, may also be found in other positions. This is necessary so that when the unit cell is propagated in three dimensions, the partial atoms at the corners can combine to make the complete atoms that compose the macroscopic crystal. The translation of the unit cell in Figure 21.5 shows that, if the same atom weren't at all corners, the unit cell would not make sense as a multidimensional crystal. This idea holds whether we are talking about simple ionic crystals like CsCl or complicated molecular crystals like crystalline naphthalene, C_8H_{10}. In order to define a unit cell, the same species in the same orientation (for molecules) must be present at the corners.

The same species (atom, ion, or molecule) may also be present in other locations about the unit cell, and they may reside at differing distances and angles depending on the dimension. CsCl, for example, has a very simple unit cell that can be illustrated as a cubic structure; other compounds are not so simply described. It can be shown that there are only 14 ways of describing how similar species (like the Cs^+ or Cl^- ions) will be arranged in three-dimensional space. These 14 structures can be grouped into seven systems depending on their symmetry elements; within each system, there can be variations in the appearance of atoms/ions/molecules at certain positions within the unit cell.

We will focus on the seven systems first; they are listed in Table 21.1. Spatially, we define the systems in terms of the dimensions of the unit cell, labeled a, b, and c (where, by convention, $a \leq b \leq c$) and the angles that these dimensions make with each other, labeled α, β, and γ. (Again, by convention, α is the angle between b and c, β is the angle between a and c, and γ is the angle between a and b. See Figure 21.8.) The simplest crystal system is when all dimensions are equal and all angles are 90°. This defines the *cubic* crystal system and is exemplified by CsCl (see Figure 21.7). There are also systems where the angles are all still 90° but one dimension of the unit cell is different from the other two (*tetragonal*) or all dimensions of the unit cell are different (*orthorhombic*).

Table 21.1 The seven basic crystal systems

Name	Unit cell dimensions	Unit cell angles
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°; \gamma = 120°$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°; \beta \neq 90°$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$

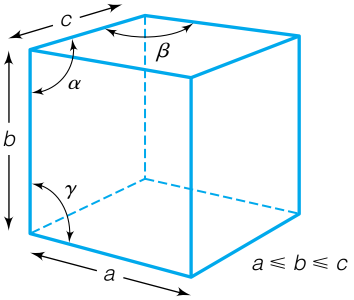


Figure 21.8 Definition of unit cell parameters. The lengths of the unit cell are labeled a, b, and c, such that $a \le b \le c$. The angles between the unit cell dimensions are α, β, and γ; they are defined as shown.

Table 21.2 The fourteen Bravais lattices

Crystal system	Bravais lattice	Symbol(s)
Cubic	Simple (or primitive) cubic	sc, P
	Body-centered cubic	bcc, I
	Face-centered cubic	fcc, F
Tetragonal	Simple (or primitive) tetragonal	P
	Face-centered tetragonal	F
Orthorhombic	Simple (or primitive) orthorhombic	P
	Body-centered orthorhombic	I
	Face-centered orthorhombic	F
	End- (or base-) centered orthorhombic	C
Trigonal[a]	Simple (or primitive) trigonal	P
Hexagonal	Simple (or primitive) hexagonal	P
Monoclinic	Simple (or primitive) monoclinic	P
	End- (or base-) centered monoclinic	C
Triclinic	Simple (or primitive) triclinic	P

[a] Trigonal is also known as rhombohedral in some texts.

Now we consider systems where the angles between a, b, and c are not all 90°. For this set we start with the least restricted case. If all distance and angle parameters are different, the crystal is *triclinic.* If two of the angles are 90° and one not, then the crystal is considered *monoclinic.* If all three unit cell dimensions are the same ($a = b = c$) and the angles are equal but not 90°, then the crystal is described as *trigonal* or *rhombohedral.* And last, some crystals have a sixfold symmetry. Such crystals are called *hexagonal.*

Finally, within some of the systems are subsystems that have additional atoms or ions or molecules. These subsystems differ only by having corner species in other parts of the unit cell, like the sides or the center of the unit cell. Table 21.2 lists these details, and Figure 21.9 shows examples of the additional possible cubic, tetragonal, orthorhombic, and monoclinic crystal structures. These 14 possible crystal structures are called the *Bravais lattices,* after the French scientist Auguste Bravais (1811–1863), who first described them in 1848.

The cubic crystal system, for example, is separated into three Bravais lattices depending on whether the unit cell has species only at the corners (*simple* or *primitive cubic*); at the corners and the center of the unit cell (*body-centered cubic*); or at the faces of the unit cell (*face-centered cubic*). Note that for the body-centered cubic, the species (atom, ion, or molecule) in the center contributes one full member to the stoichiometry of the cell, and the atoms, ions, or molecules in the faces of the unit cell contribute $\frac{1}{2}$ of a member *each.* (Recall that species at the corners contribute $\frac{1}{8}$ of a member each.) For face-centered cubic unit cells, the facial species contribute, overall, $\frac{1}{2} \times 6 = 3$ members to the stoichiometry of the unit cell.

The tetragonal system can also have species in the center of the unit cell. Orthorhombic crystals can have species in the center (body-centered), in all faces (face-centered), only in opposing faces (end-centered), or only at the corners (primitive). Monoclinic unit cells can be either primitive or end-centered, with species in one set of opposing faces. Triclinic, hexagonal, and trigonal unit cells are just primitive.

Table 21.2 also lists another standard nomenclature for referring to the types of Bravais lattice. Generally, the letter P is used to indicate a primitive lattice, I is used for body-centered lattices, F for face-centered lattices, and C for end-centered lattices.

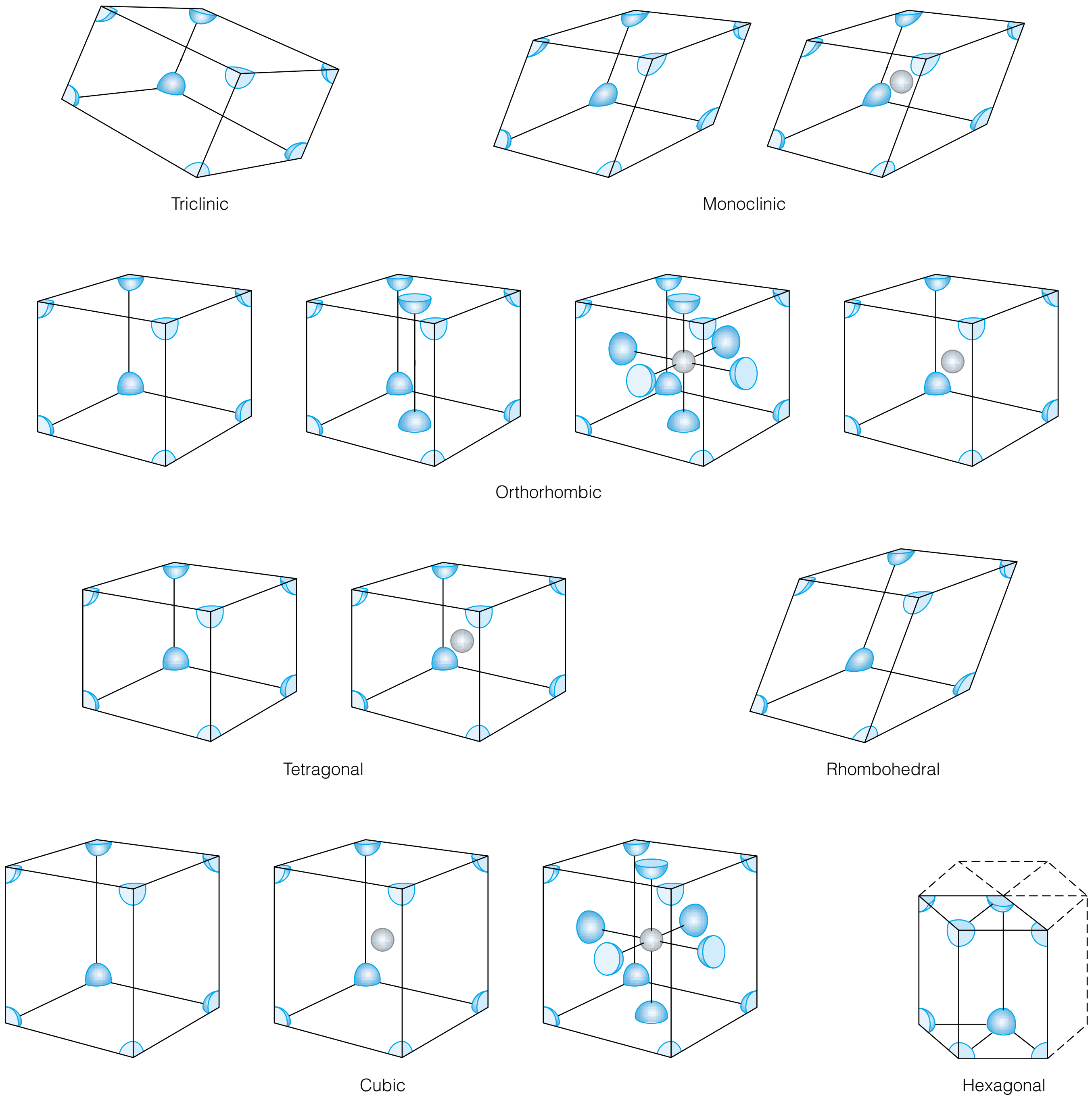


Figure 21.9 The 14 Bravais lattices that are possible for the seven crystal systems. Some crystal systems have more than one possible lattice; others have only one.

It might seem that 14 lattices are not enough to describe the possible arrangements of crystals that might exist. However, they do cover all possibilities. By its very definition, a crystal has a specific three-dimensional symmetry, and these 14 lattice types cover all possible three-dimensional symmetry arrangements. Also, if you were to add an atom to a center or face of a lattice in an attempt to define a new Bravais lattice, you would make a crystal whose true Bravais lattice can be described by a different (and usually smaller!) unit cell that would be one of the 14 lattices described.

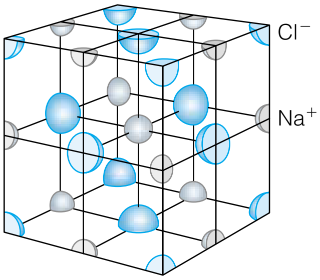


Figure 21.10 A unit cell for sodium chloride, NaCl. See Example 21.1.

Example 21.1

Figure 21.10 shows a unit cell for NaCl, another simple ionic crystal.
a. Identify the Bravais lattice for NaCl.
d. Determine the stoichiometry of the unit cell. Is it consistent with the formula of this compound?

Solution

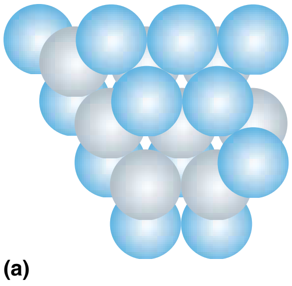
a. First, we should confirm that the same species is present at all corners. Checking Figure 21.10, we see that there are Cl^- ions at all corners. (This is a point that many people do not understand when trying to define the unit cell for a crystal!) Next, we try to identify Cl^- ions at other points in the unit cell. Cl^- ions are also located in all six faces of the unit cell. Therefore, we would assign a face-centered cubic Bravais lattice to NaCl.
b. The corners contribute $\frac{1}{8} \times 8 = 1$ atom of Cl, overall, to the formula of the compound, and the faces contribute $\frac{1}{2} \times 6 = 3$ atoms of Cl. One Na^+ ion is in the center of the unit cell, and on each edge of the unit cell an Na^+ ion contributes $\frac{1}{4}$ of the atom to the unit cell. (Do you see this? Refer to Figure 21.10 and show that only $\frac{1}{4}$ of each Na^+ ion actually resides in the unit cell.) The 12 edge Na^+ ions therefore contribute $\frac{1}{4} \times 12 = 3$ sodiums. Adding the 1 Na^+ in the center, we get a total of 4 Na^+ ions in the unit cell. Considering the Na and Cl contributions together, we have a stoichiometry of Na_4Cl_4, which in the lowest ratio reduces to NaCl: the expected formula for sodium chloride. (Note: students who just read this and did not actually refer to Figure 21.10 and make these observations on their own will have learned nothing from this example!)

Example 21.2

Explain why the CsCl unit cell is considered simple cubic and not body-centered cubic despite having an atom in the center of the unit cell. Refer to Figure 21.7 for the unit cell of CsCl.

Solution

Identification of a unit cell requires that the *same* species—whether atom, ion, or molecule—be present at the proper positions in the unit cell. In the case of CsCl, there are Cs^+ ions at the corners, which is the minimum requirement for any unit cell, but no Cs^+ ions in the center (it's a *Cl^- ion*). Therefore, the presence of the Cl^- ion does not factor into the determination of the type of unit cell, and the Bravais lattice is identified as a simple cubic lattice and not a body-centered cubic lattice.



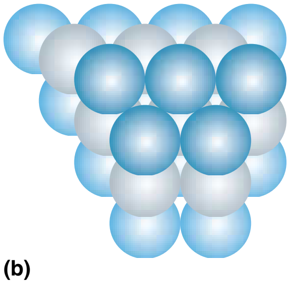


Figure 21.11 Two different ways of getting the most efficient packing of spherical atoms. (a) Using the bottom layer as a base, the second layer of atoms lies in the dips made by three adjacent base atoms. In the third layer, atoms lie in dips created by the second layer, but they also lie directly above atoms of the first layer. This is the ABAB . . . pattern of close-packing. (b) In this case, atoms in the third layer do not lie directly above the first layer's atoms, but rather in different relative positions. This is the ABCABC . . . pattern of close-packing.

Two crystal lattices deserve some special mention. Consider a monatomic crystal composed of atoms all the same size. What is the most space-efficient way to make them into a crystal? Figure 21.11 shows two different ways of placing atoms most efficiently. On the bottom layer of each diagram, atoms make a nice, regular lattice. The next-to-bottom layer lies in the natural dips created by three adjacent, triangularly spaced bottom-row atoms.

For the third layer, there is a choice. On the one hand, and perhaps the easier choice to illustrate, the atoms in the third layer can be placed directly above the atoms in the first layer, as shown in Figure 21.11a. Building the crystal can be continued by repeating each layer's position accordingly. If the first layer is labeled A and the second layer B, we can indicate the building of this crystal as alternating layers of A, B, A, B, ...

On the other hand, the third layer of atoms could be placed in positions that are different from layer A or layer B; this is shown in Figure 21.11b and the layer is usually labeled as layer C. In this crystal, the alternating layers can be listed as A, B, C, A, B, C, ...

Both arrangements are the most space-efficient ways of packing atoms, ions, or molecules. Figure 21.12a shows that the ABAB form of crystal has a hexagonal Bravais lattice. The ABCABC . . . form of crystal has a face-centered cubic Bravais lattice (see Figure 21.12b). Both of these crystal lattices represent the most space-efficient form of crystal; over 50 of the elements themselves, from noble gases to metals, have either hexagonal or face-centered cubic crystal lattices in their solid form. Because of the efficiency of the hexagonal crystal lattice, it is sometimes called the *hexagonal close-packed* (or *hcp*) lattice.

These space-efficient crystal structures also show up in the real world of macroscopic objects. For example, stacks of golf balls, basketballs, or baseballs mimic an hcp or face-centered cubic arrangement. At grocery stores, fruits or vegetables that are roughly spherical (oranges, apples, pears, citrus fruits) can be stacked in a close-packed arrangement. Figure 21.13 shows an example of this. This arrangement is used for its stability and, again, its efficient use of space.

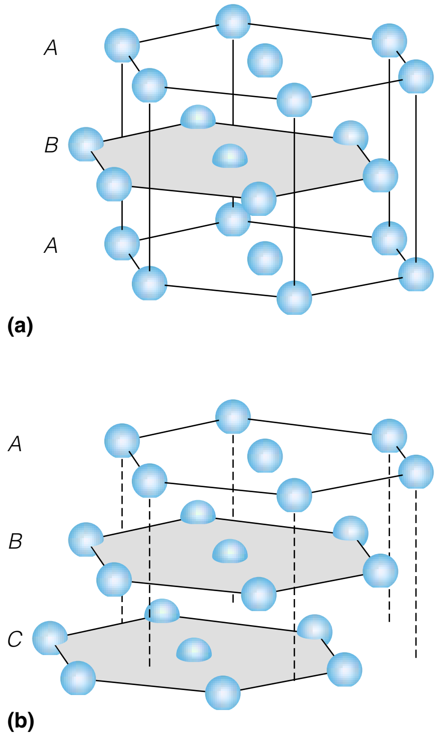


Figure 21.12 (a) The hexagonal unit cell for the ABAB . . . pattern of close-packing. (b) The face-centered cubic unit cell for the ABCABC . . . pattern of close-packing.

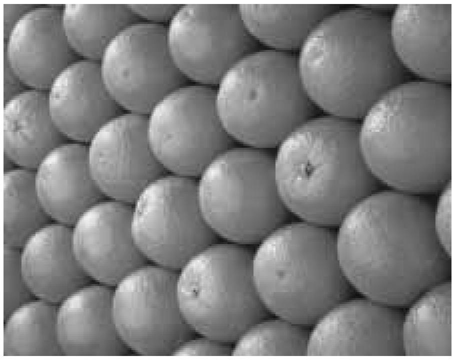


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Figure 21.13 Close-packed arrangements in solids are easily mimicked in macroscopic arrangements, like this fruit display. Can you tell if this "crystal" would have a hexagonal or face-centered cubic unit cell?

21.4 Densities

Knowledge of the crystal lattice designation of a crystal implies that we know how many molecules are in the unit cell. If we have the unit cell parameters (that is, the three distance parameters a, b, and c, and the three angular parameters α, β, and γ) we can calculate the density of the compound. Comparison of the calculated density with an experimentally determined density should yield the same value. (In fact, agreement between calculated densities and experimental densities was perhaps a final—though unnecessary—supporting argument for the atomic theory of matter.)

Recall that density is defined as mass per unit volume:

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{21.1}$$

Typically, the density of solids is given in units of grams/milliliter, abbreviated g/mL; since a milliliter is equal to a cubic centimeter, densities are also commonly expressed in units of g/cm^3. A unit cell, however, is very small: typically on the order of angstroms on a side (where $1\ \text{Å} = 1 \times 10^{-10}$ m). Also, in a unit cell we are considering (usually) a small number of atoms or molecules per unit cell. The total mass of any one unit cell is therefore very small in an absolute sense, on the order of 10^{-26} to 10^{-27} kg. In fact, it is typical to use the unit "atomic mass unit," or amu, to describe masses of individual atoms and molecules. The amu is defined as

$$1\ \text{amu} = 1.6605 \times 10^{-27}\ \text{kg} \tag{21.2}$$

Thus, we have for a single unit cell

$$\text{density} = \frac{\text{mass}}{\text{volume}} \quad \text{in units of } \frac{\text{amu}}{\text{Å}^3}$$

Luckily, going from amu/Å^3 to g/mL is simply an exercise in unit conversions. We can use equation 21.2 along with the fact that

$$1 \text{ mL} = 1 \text{ cm}^3 = 10^{24} \text{ Å}^3 \qquad \textbf{(21.3)}$$

to determine a macroscopic density in measurable units from a microscopic density in terms of unit cell parameters.

The masses of the atoms and molecules are taken from the cumulative number of atoms or molecules in the unit cell. The volume of the unit cell is determined from geometry. From geometry, the equation that gives the volume of a six-sided object with parallel opposing faces (called a *parallelepiped*) is

$$\text{volume} = a \times b \times c \times \sqrt{(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)} \qquad \textbf{(21.4)}$$

Equation 21.4 is general; the user should recognize that for some crystal lattices, two or three sides of the unit cell may have the same length, and two or three of the angles may also be the same (that is, 90°). The definitions of the angles α, β, and γ with respect to the lattice sides should also be remembered. For a unit cell that has 90° angles, equation 21.4 reduces to

$$\text{volume} = a \times b \times c$$

as it should for a right-angle solid. Examples 21.3 and 21.4 show how to relate macroscopic densities and microscopic information.

Example 21.3

Solid silver exists as a face-centered cubic crystal with $a = 4.09$ Å. What is the density of silver? Assume that each silver atom has a mass of 108 amu.

Solution

First, we must determine the number of silver atoms in a face-centered cubic unit cell. Each corner atom contributes $\frac{1}{8}$ of an atom to each unit cell. There are eight corner atoms, contributing a total of $\frac{1}{8} \times 1 = 1$ silver atom. Each face contributes $\frac{1}{2}$ of an atom to each unit cell. Overall, the six faces of the cubic lattice add $\frac{1}{2} \times 6 = 3$ silver atoms to each unit cell. Each cell therefore has $3 + 1 = 4$ silver atoms per cell. If each silver atom has a mass of 108 amu, then the total mass of each unit cell would be four silver atoms:

$$\text{mass} = 4 \times 108 \text{ amu} = 432 \text{ amu}$$

The volume of the unit cell can be determined using equation 21.4, in part by recognizing that in a cubic cell the angles are all 90°:

$$\text{volume} = a \times b \times c = 4.09 \text{ Å} \times 4.09 \text{ Å} \times 4.09 \text{ Å}$$

$$\text{volume} = 68.4 \text{ Å}^3$$

Using the definition of density and converting to its more common units:

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

$$= \frac{432 \text{ amu}}{68.4 \text{ Å}^3} \times \frac{1.6605 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \times \frac{10^{24} \text{ Å}^3}{1 \text{ cm}^3} \times \frac{1000 \text{ g}}{1 \text{ kg}}$$

$$\text{density} = 10.5 \text{ g/cm}^3$$

The measured density of silver is 10.5 g/cm^3, exactly the same (to three significant figures) as the calculated density.

Example 21.4

Solid nitrogen, N_2, has a density of 1.026 g/cm^3 at about 20 K. If solid nitrogen is known to have some cubic lattice with a length of 5.66 Å, what kind of cubic lattice does solid N_2 have?

Solution

From the length of the lattice, we can determine the volume of the unit cell:

$$\text{volume} = (5.66\ \text{Å})^3 = 181\ \text{Å}$$

From the known density (and a few unit conversions), we can now determine the amount of mass in each unit cell:

$$\text{mass} = \text{density} \times \text{volume}$$

$$= 1.026\frac{\text{g}}{\text{cm}^3} \times 181\ \text{Å}^3 \times \frac{1\ \text{amu}}{1.6605 \times 10^{-27}\ \text{kg}} \times \frac{1\ \text{cm}^3}{10^{24}\ \text{Å}^3} \times \frac{1\ \text{kg}}{1000\ \text{g}}$$

$$\text{mass of unit cell} = 112\ \text{amu}$$

Each nitrogen molecule, with two nitrogen atoms each, has a mass of 28 amu. If there are 112 amu per cell, then there are

$$\frac{112\ \text{amu per cell}}{28\ \text{amu per N}_2} = \frac{112\ \text{amu/cell}}{28\ \text{amu/N}_2} = \frac{4\ \text{N}_2}{\text{cell}}$$

or 4 nitrogen molecules per unit cell. (Note how the units work out algebraically.) The type of cubic Bravais lattice that has four species per unit cell is the face-centered cubic lattice, which has $\frac{1}{8}$ of a species at each of eight corners (1 molecule overall) and $\frac{1}{2}$ of a species at each of six faces (3 molecules overall) for a total of 4 molecules per unit cell. We therefore predict that solid N_2 has a face-centered cubic lattice.

The two previous examples used cubic crystals, which are easier to visualize because of their perpendicular sides. Noncubic crystals are treated similarly.

Photograph by Francis Simon, Courtesy AIP Emilio Segre Visual Archives

Figure 21.14 Max von Laue (1879–1960) was a German physicist who originally proposed that crystals, if they were indeed made up of atoms, should act as gratings to diffract X rays. He was right, and he won the 1914 Nobel Prize in physics as a result.

21.5 Determination of Crystal Structures

How do we know what the crystal lattices are for elements, molecules, and compounds? The answer is an interesting historical story.

In the late 1800s, scientists were finally realizing that what we call light was not just visible light but included a lot of invisible light, too. Light could be thought of as a wave that had varying frequency and wavelength. On the very short-wavelength and high-energy side of "light" (now better referred to as electromagnetic radiation) are the X rays, originally named by the German physicist and discoverer Wilhelm Roentgen in 1895 because of their unknown nature. X rays were ultimately shown to be a form of electromagnetic radiation having very short wavelength, generally considered to be between 0.01 and 100 Å.

At the same time, it was known to physical science that a series of equally spaced parallel grooves in a mirrored surface, called a *grating*, could diffract light just like a prism could. This effect was especially pronounced if the grooves were spaced on the order of the wavelength of the light. (Indeed, most modern dispersive spectrometers use a grating as the *dispersive element*. Details of instrumentation can be found in analytical chemistry or instrumental analysis textbooks.) Matter is usually relatively transparent to X rays to different degrees; this characteristic is what makes X rays useful for medical purposes. But in or around 1912, the German physicist Max von Laue (Figure 21.14) reasoned that in crystals, the rows of atoms (or ions or molecules) were spaced at distances that corresponded to the wavelength of X rays, so crystals should *diffract* X rays. In 1912, experiments with crystals of copper sulfate and, later, zinc sulfide confirmed this idea.

This result was furthered by von Laue and also by the father-and-son team of William Henry Bragg (Figure 21.15a) and William Lawrence Bragg (Figure 21.15b). In particular, in 1915 the Braggs worked out a simple relationship between the wavelength, λ, of monochromatic X rays that are preferentially diffracted by a crystal lattice, the distance, d (sometimes called the *d spacing*), between the planes that the crystal lattice makes, and the angle, θ, between the crystal planes and the incoming monochromatic X rays. The relationship is

$$n\lambda = 2d \sin \theta \tag{21.5}$$

where n is an integer (0, 1, 2, 3, and so on). Equation 21.5 is known as *Bragg's law of diffraction.* For their work on X rays and crystals, von Laue won the 1914 Nobel Prize in physics and the two Braggs won the next year's prize. (The younger Bragg was only 25 at the time and still holds the record for the youngest Nobel laureate. The Braggs' award-winning work had just been published earlier that year.)

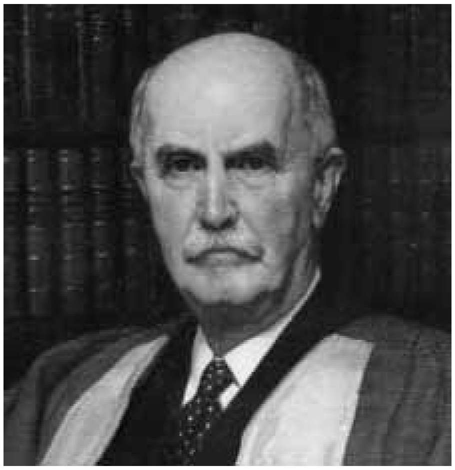
If n equals 0, the process is equivalent to reflection of light at a surface, which is not a new physical phenomenon; it will not be considered further. If n equals 1, then X rays will be preferentially diffracted only if their wavelength is equal to $2d$ times the sine of the angle the X rays make with the plane of the crystalline species:

$$\lambda = 2d \sin \theta \tag{21.6}$$

The physical reason for this preferential diffraction is shown in Figure 21.16. If monochromatic X rays were approaching a crystal (which again is normally very transparent to X-ray radiation) at some random angle (Figure 21.16a), then radiation reflected from multiple planes of crystalline species would combine *destructively* and no coherent, measurable diffracted X rays would be produced.

On the other hand, if the angle θ is just right, then the X rays reflected from multiple planes would *constructively* interfere, and the X ray would be diffracted, as shown in Figure 21.16b. A detector at just the right angle would measure X rays coming from the crystal as the crystalline lattice diffracts the radiation. The 2 is present in equations 21.5 and 21.6 because the radiation must travel twice the distance between the diffracting layers. The mathematical relationship between λ and θ can actually be derived from geometric principles (which is what the Braggs did). In Figure 21.16, because there is only one wavelength of light between adjacent layers of crystal, n equals 1 and this diffraction is called *first-order diffraction.* (Unless otherwise stated, we will assume that a diffraction of X rays from crystal is a first-order diffraction.)*

The more general form of Bragg's law, equation 21.5, allows for different, but *integral,* numbers of wavelengths of X rays to satisfy this constructive


(a)

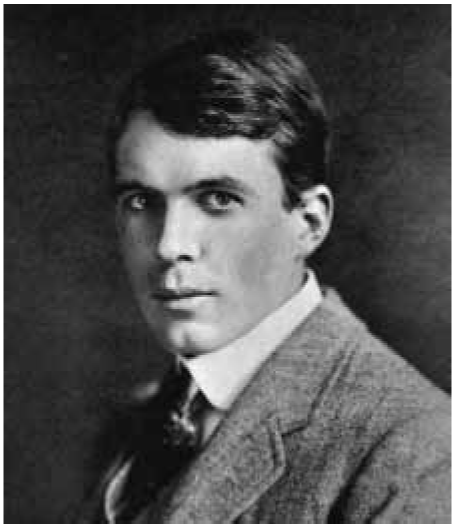

(b)

Figure 21.15 William Henry Bragg (1862–1942) and William Lawrence Bragg (1890–1971) were the father-and-son team that took von Laue's idea and expressed it in a simple mathematical form so it could be applied to any crystalline solid. Their Nobel Prize in physics followed the year after von Laue's. At an age of 25 years, William Lawrence Bragg is the youngest person to be named a Nobel laureate.

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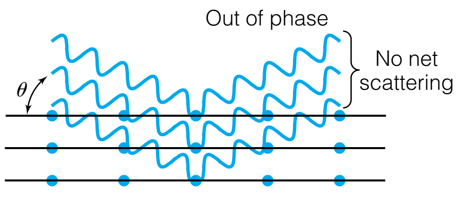
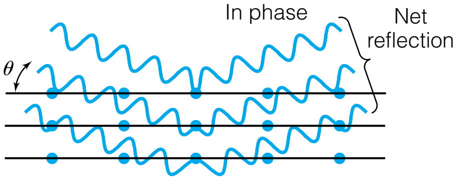
*Destructive interference can also occur between reflections off different planes that are a distance of $\lambda/2$ apart. For example, in face-centered cubic crystals, some diffractions that satisfy Bragg's law are not detected because of these destructive interferences.



(a) Destructive interference



(b) Constructive interference

Figure 21.16 (a) At any random angle, X rays that reflect off sequential layers of atoms in a crystal destructively interfere to yield, ultimately, no net intensity of refracted X rays. (b) If the relationship between angle, X-ray wavelength, and spacing between the layers of atoms is just right, there are an integral number of wavelengths between the distance traveled by X rays and there is *constructive* interference: a strong diffraction of X-radiation occurs. The relationship between angle, X ray wavelength, and *d* spacing is called the Bragg equation. This equation includes the possibility that there may be more than one wavelength between adjacent reflections; this is the *order* of the diffraction.

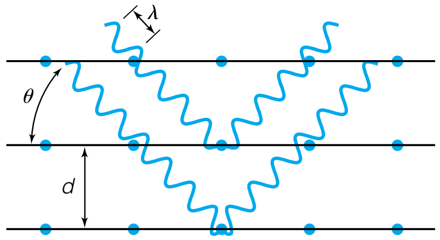


Figure 21.17 When there are two (or more) additional wavelengths between adjacent reflections of X rays, it is considered second- (or higher-) order diffraction. In this case, the variable *n* in the Bragg equation equals 2.

interference condition. Figure 21.17 shows that the same wavelength of X rays as in Figure 21.16b will be diffracted at a different angle because now n equals 2: this is called second-order diffraction. There is also third-order diffraction ($n = 3$), fourth-order diffraction ($n = 4$), and so on. The first-order diffraction is usually the most obvious, although depending on the crystal the zeroth-order diffraction ($n = 0$, simple reflection) may also be very obvious.

The following examples illustrate the use of Bragg's law.

Example 21.5

A simple cubic lattice has atoms that are spaced by 2.77 Å. If the diffraction is caused by planes of atoms that are 2.77 Å apart, at what angle are X rays diffracted in the first order and the second order if they have a wavelength of 1.82 Å?

Solution

Notice that the X-ray wavelength and the distance between diffracting planes are given in the same units, angstroms. This is important, since these are the only quantities in Bragg's law that have units. For first-order diffraction, we use equation 21.6:

$$\lambda = 2d \sin \theta$$

$$1.82\ \text{Å} = 2(2.77\ \text{Å}) \times \sin \theta$$

The only variable is the angle θ:

$$\frac{1.82\ \text{Å}}{2 \times 2.77\ \text{Å}} = \sin \theta$$

Again, notice that the units of Å cancel algebraically. We get

$$\sin \theta = 0.329$$

Taking the inverse of the sine function of both sides, we find that

$$\theta = 19.2°$$

So the angle in Figure 21.16b would be 19.2° in this case. At all other angles, destructive interference takes place and virtually no intensity of X rays is detectably diffracted.

For the second-order diffraction, we must use $n = 2$:

$$2\lambda = 2d \sin \theta$$

(It was assumed that n is 1 in the first part, so it did not show up in the expression for Bragg's law.) We get

$$2 \times 1.82\ \text{Å} = 2(2.77\ \text{Å}) \times \sin \theta$$

$$\frac{2 \times 1.82\ \text{Å}}{2 \times 2.77\ \text{Å}} = \sin \theta$$

$$\sin \theta = 0.657$$

Again, note that the units cancel. Taking the inverse sine of both sides, we find

$$\theta = 41.1°$$

Notice that the angle of the second-order diffraction (41.1°) is *not* double the angle of the first-order diffraction (19.2°). That's because the order of diffraction is dependent on the sine of the angle, not the angle itself.

Example 21.6

Monochromatic X rays having a wavelength of 10.4 Å are preferentially diffracted by a crystal at an angle of 25.5°.

a. Assuming that this is the first-order diffraction, what is the d spacing between the crystalline planes?

b. At what angle would the second-order diffraction be found?

Solution

a. For $n = 1$ (that is, first-order diffraction), we can set up Bragg's law as

$$10.4\ \text{Å} = 2d \sin(25.5°)$$

and the only unknown in this equation is d, the spacing between crystalline planes. Solving for d:

$$d = \frac{10.4\ \text{Å}}{2 \sin(25.5°)}$$

$$d = 12.1\ \text{Å}$$

Notice how the units work out: the only unit is a unit of distance, Å.

b. Knowing the value for d, we can find the angle for the second-order diffraction of these X rays. In this case, $n = 2$, and we can set up Bragg's law as

$$2(10.4\ \text{Å}) = 2(12.1\ \text{Å}) \sin\theta$$

Now the angle θ is the only unknown in the expression. Solving for $\sin\theta$:

$$\sin\theta = \frac{2(10.4\ \text{Å})}{2(12.1\ \text{Å})}$$

$$\sin\theta = 0.859$$

$$\theta = 59.3°$$

Notice that mathematically, only so many orders of diffraction may be possible for any given spacing of crystal planes and a given X-ray wavelength. In the previous example, if you were trying to determine the angle of the third-order diffraction, you would get to the expression

$$\sin\theta = \frac{3(10.4\ \text{Å})}{2(12.1\ \text{Å})}$$

where the 3 in the numerator represents the order n. Evaluating this fraction, we get

$$\sin\theta = 1.289$$

Sine functions can't get above a value of 1, so having a sine of 1.289 is physically impossible. This shows that the given plane of atoms can diffract 10.4-Å X rays only to the first and second order.

Although Bragg's law is the fundamental basis of experimental crystallography, its simplicity is potentially misleading. For the simplest of cubic lattices (like many of the solid noble gases), only one type of atom can make a plane that refracts X rays. Consider a molecular crystalline solid like water, H_2O: not only is the crystal more complicated because it's a molecular solid, but each atom in the molecule can be used to define a regular matrix of atoms that can act as a refracting plane. The diffraction of X rays by any random compound is in fact very complex because most compounds, being molecular, will have many atoms in corresponding unit-cell positions that can contribute to diffractions.

There is an additional complication depending on the sample's form: that of crystal orientation. A sample of material that exists as one single crystal has specific unit cell orientations. The refractions of X rays will also have certain specific orientations (thanks in part to Bragg's law), and experimental determinations of X-ray diffractions use that specificity to determine the structures of compounds; computers are extremely useful in back-calculating a molecular structure from the angles of X-ray diffraction. However, if the sample is powdered or polycrystalline, each tiny crystal in a sample has its own orientation with respect to the incoming X rays, and so will impose its own unique direction to the outgoing, diffracted X rays. X-ray diffraction patterns of powdered samples are usually much more complicated than those of single crystal X-ray diffractions, although the so-called powder patterns are typically easier to obtain experimentally. (The exception is for cubic unit cells; because the unit cells are cubic, it does not matter what orientation each tiny microcrystalline fragment has.) As you might expect, scientists who perform X-ray diffraction prefer single-crystal samples to determine the molecular structure of a compound. This can be difficult to provide, especially if the compound is a large biomolecule that is hard to crystallize.

21.6 Miller Indices

The previous section considered diffractions of X rays as if they were done by a single layer of atoms in a crystal. Actually, they aren't, as illustrated by Figure 21.16: diffractions are caused by the constructive interference of reflections of X rays by sequential planes of atoms in similar unit-cell positions throughout the crystal. The collection of planes actually makes X-ray diffraction a three-dimensional phenomenon (even though Figure 21.16 shows it in two dimensions).

However inaccurate the depiction, the idea of X-ray diffraction does bring up the concept that planes of atoms are important in an understanding of crystal structures. In the first approximation, individual planes of atoms reflect X rays, and the constructive interference of many reflections from many planes yields refraction of X rays at the right angle. How do we define a plane of atoms in terms of the unit cell? There is another consideration, too: at some point, the supposed infinite array of unit cells must, in fact, stop and make the surface of the crystal. This surface is usually considered planar. (In fact, many examples of large crystals are used as examples because they have well-defined planar surfaces. A well-cut diamond, for example, has a very specific shape in terms of the planes that terminate the unit cells.) It becomes clear that we must be able to define planes of corresponding atoms within arrays of unit cells.

We use *Miller indices* to label the different possible planes that corresponding species can make. (Recall that *indices* is the plural of *index*. Although this system was originally established by William Whewell in 1825, it was popularized in an 1839 crystallography text by William Miller, an English mineralogist.) Miller indices are based on the unit cell dimensions a, b, and c acting as unit vectors. They are also *reciprocal indices* in that they relate to the reciprocal of the fraction or multiple of unit vectors along each axis where any given plane intersects.

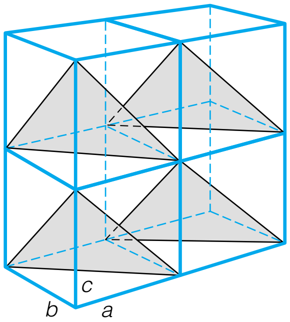


Figure 21.18 How to determine Miller indices of parallel planes of atoms. See text for details.

Figure 21.18 shows the steps in determining the Miller indices of a plane in a simple cubic unit cell. (The process is the same for other unit cells; it just looks more complicated.) In the four unit cells shown, parallel planes of atoms are indicated. How do we designate these parallel planes in terms of the unit cell dimensions *a*, *b*, and *c*? We use the following steps:

1. Using any unit cell, pick a corner that will serve as a three-dimensional, Cartesian-axis origin. An example is indicated in Figure 21.18.
2. Determine the intercepts of the planes in terms of how many *a*, *b*, and *c* units the intercepts are from the origin. In Figure 21.18, the indicated plane intercepts the crystal axes at 1 *a* unit, 1 *b* unit, and 1 *c* unit of length in each of the crystal dimensions. The numbers we collect to represent the indicated plane are 1, 1, and 1—indicating the number of unit cell dimensions that represent the axes' intercepts.
3. Take the reciprocal of each number: in this case, the reciprocals of 1, 1, and 1 are simply 1, 1, and 1 (but we will consider another example next).
4. Express the Miller indices as the three reciprocal numbers grouped together inside parentheses, without punctuation: (111). The plane illustrated in Figure 21.18 is referred to as the (111) plane for this simple cubic lattice.

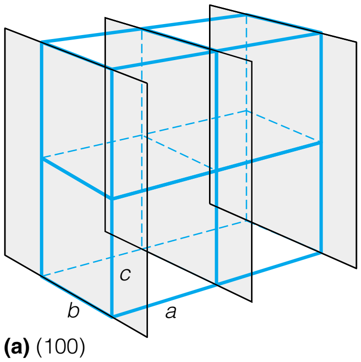
The Miller indices for any plane of crystal positions can be determined by this method. The general form of expressing Miller indices is ($hk\ell$), where h represents the Miller index along the *a* unit cell dimension, k is the Miller index along the *b* unit cell dimension, and ℓ is for the *c* unit cell dimension. For cubic unit cells, there are equivalences among planes that have the same Miller indices, such that (100) is equivalent to (010), which is equivalent to (001), and so forth.

There are several pitfalls to watch out for. First, there are (maybe obvious) planes that are in one of the planes of the unit cell itself: Figure 21.19 shows several. None of these planes intersects the third crystal axis. In this case, the intercepts are considered to occur at infinite dimensions of the unit cell, and the reciprocal of ∞ is zero: therefore, the Miller indices of the planes in Figure 21.19 are (100), (110), and (200), respectively. (You should satisfy yourself that these designations are correct.)

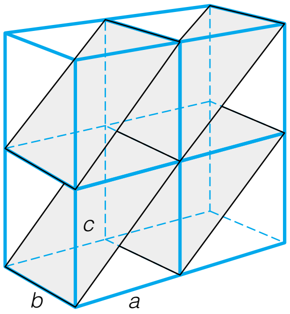
Second, Miller indices can also be numbers greater than 1 (usually integers) or less than 1 (usually a simple fraction). Figure 21.19c shows a plane of crystal positions that includes an index greater than 1. Again, you should satisfy yourself that the steps given above give corresponding Miller indices.

Finally, Miller indices are occasionally best described using negative numbers. But given the lack of punctuation in the expression (ABC) for a crystal plane, using a minus sign might cause a problem with interpretation; consider (A − BC) as a label for a crystal plane! Rather, it is the convention to put a bar over a Miller index to indicate that it is negative: rather than (A − BC), we write ($A\bar{B}C$), where $\bar{B}$ indicates that the Miller index (as determined from the steps above) is actually −B. Figure 21.20 shows an example of a crystal plane defined this way.

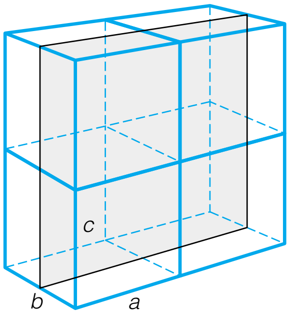
Why do we go to such trouble? Because each and every definable plane can act to diffract X rays to produce constructive interference of radiation. Since different planes have different *d* spacings, planes having different Miller indices will diffract the same X rays at different angles. As we use the phenomenon of constructive radiation to understand the structures of crystals, we need a system to keep track of the planes of atoms (molecules, ions, and so on) that are reflecting the radiation. The concept of Miller indices shows that there are



(a) (100)



(b) (110)



(c) (200)

Figure 21.19 Miller indices of some planes in cubic crystals.

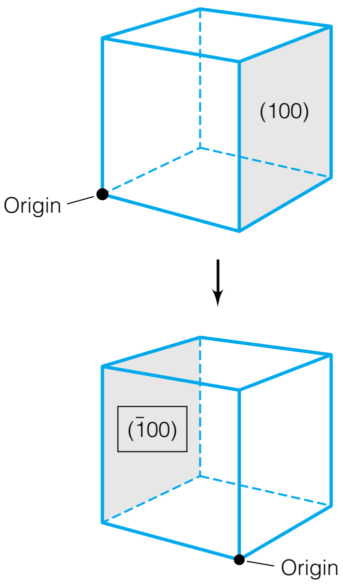


Figure 21.20 This diagram shows how the (100) plane can be defined using negative Miller indices.

many possible planes, which suggests that X-ray crystallography is rather complicated. In some cases it is; but Miller indices give us a way to model how different crystal planes can interact with radiation.*

Example 21.7

Assuming that there are atoms at the proper positions in the crystal, determine the Miller indices of the plane illustrated in Figure 21.21. The fact that the crystal is not cubic is irrelevant! Notice also that only a single unit cell is shown.

Solution

We will use the lower left-hand corner as our origin. The indicated plane intercepts the *a*, *b*, and *c* crystal axes at 1 unit of *a*, 1 unit of *b*, and $\frac{1}{2}$ unit of *c*. Taking the reciprocal of the number of unit vectors, we get $\frac{1}{1}$, $\frac{1}{1}$, and $\frac{1}{1/2}$ as the Miller indices, or 1, 1, and 2 (respectively). We therefore express the Miller indices of this crystal plane as (112).

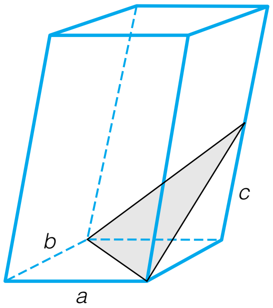


Figure 21.21 Atoms in the indicated plane have what Miller indices? See Example 21.7.

Example 21.8

Cesium chloride, CsCl, has a simple cubic lattice that has a lattice parameter of 4.11 Å. What wavelength of radiation is primarily diffracted at an angle of 20.0° by the (111) plane of CsCl?

Solution

This is a simple question, but it brings together several ideas. We will apply Bragg's law in a straightforward fashion, but first we must determine the distance, the *d* spacing, between the parallel (111) planes of CsCl. In order to do that, we need to use geometry to determine *d* spacings from the lattice parameter. Figure 21.22 shows the sequential steps. From Figure 21.22, we find that the *d* spacing between parallel (111) planes is 2.91 Å. Using Bragg's law:

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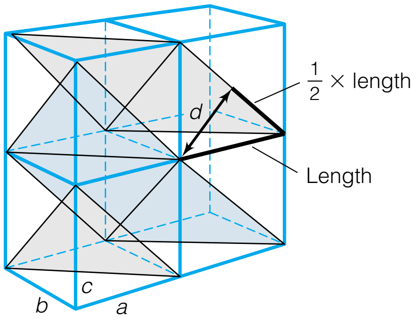
*For fcc crystals, the (100) planes experience destructive interference of diffracted X rays, so no net radiation is diffracted. This phenomenon is called *systematic extinction.* The (110) and (210) planes in fcc crystals also experience extinction. See Table 21.3 later in this section for additional planes that exhibit extinction.



Step 1. length = 4.11 Å × $\sqrt{2}$ = 5.81 Å

Step 2. $\frac{1}{2}$ (length) = $\frac{1}{2}$ (5.81 Å) = 2.91 Å

Step 3. *d* = one leg of right triangle
(the triangle indicated by bold lines)
Other leg = 2.91 Å,
hypotenuse = 4.11 Å

Using Pythagorean theorem:
$(4.11\ \text{Å})^2 = (2.91\ \text{Å})^2 + d^2$
$8.424\ \text{Å}^2 = d^2$
$d = 2.91\ \text{Å}$

Figure 21.22 Determining the diffraction of X rays using Miller indices. Application of a little geometry lets us calculate the *d* spacing from the unit cell parameters. Then we can use the Bragg equation. See Example 21.8.

$$1 \cdot \lambda = 2(2.91\ \text{Å}) \cdot \sin 20.0°$$

$$\lambda = 1.99\ \text{Å}$$

The (111) plane will diffract X rays having a wavelength of 1.99 Å at an angle of 20.0°. Notice that this wavelength is smaller than the lattice parameter itself. This is a consequence of the shorter *d* spacing that angled planes of atoms in a crystal have.

The above example should make an important point: all planes of atoms or ions in a crystal can serve to diffract X rays, not just the simple planes made by the corners of the repeating unit cells. This suggests that the diffraction of X rays by any real crystal can be very complex. It is. Figure 21.23 shows the

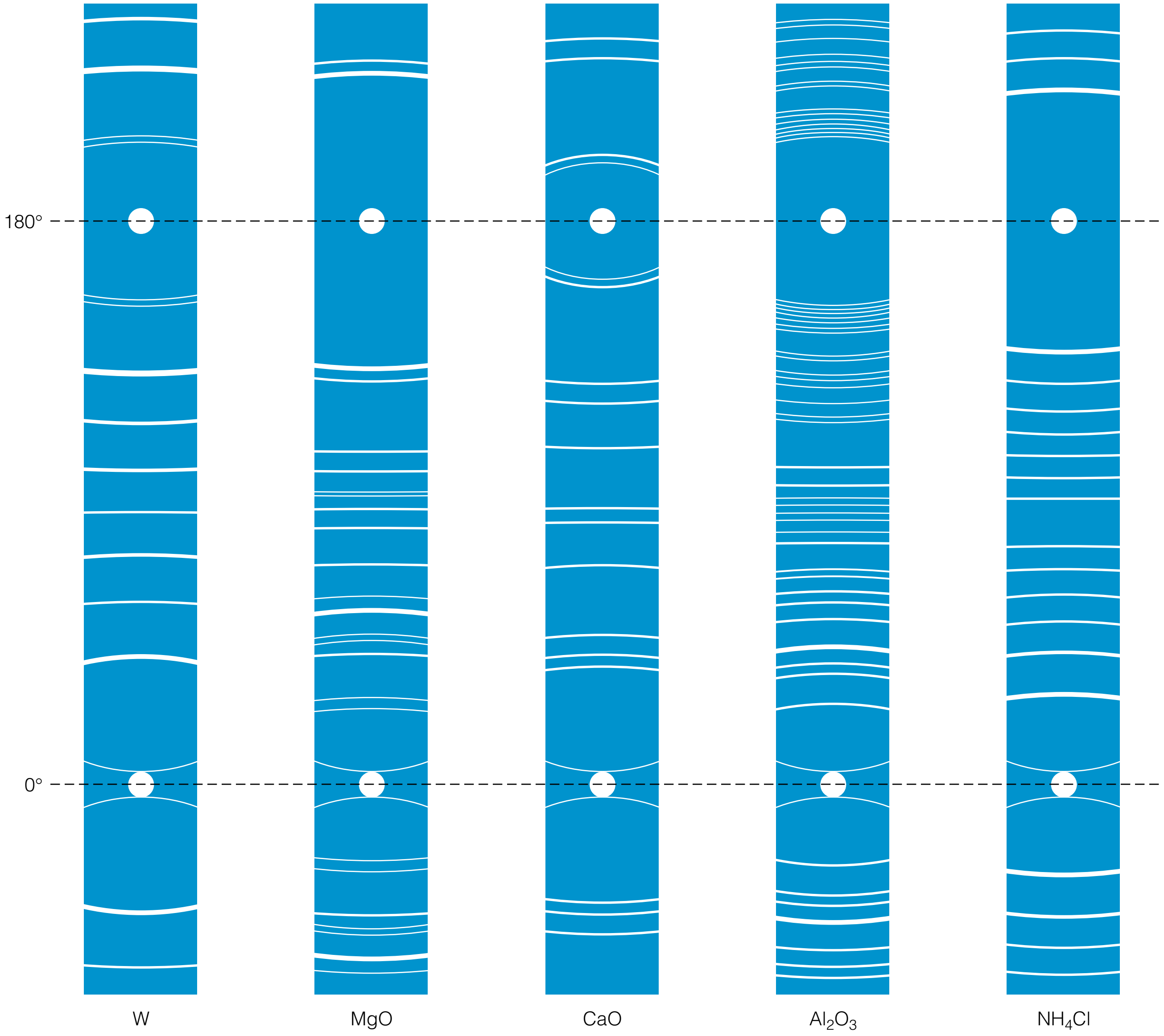


Figure 21.23 Examples of the diffraction of X rays by powdered crystals. Each strip is a piece of photographic film, encircling the powdered sample, that is exposed only at the certain angles that X rays are diffracted.

diffraction of X rays by several simple powdered compounds that have varying Bravais lattices. The different planes with their different Miller indices diffract X rays at different angles. (In practice, the X rays used are usually very close to monochromatic, which means that λ is the same for all diffractions. Only the *d* spacings between the planes and the angles of diffraction differ.) Even for simple crystals, X-ray diffraction patterns are complicated enough that computer analysis is useful.

The angles of X-ray diffraction can, however, be expressed in terms of the Miller indices (which are fractions or multiples of the unit cell dimensions, after all). The relationship between the Miller indices and the various planes of reflection is simplest for crystals having perpendicular unit cell axes, as might be expected. Without deriving it, the relationship between *d* spacing and Miller indices of a plane of atoms is

$$\frac{1}{d} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{\ell^2}{c^2}\right)^{1/2} \tag{21.7}$$

This expression is useful for cubic, orthorhombic, and tetragonal crystals. For cubic crystals, equation 21.7 can be simplified because $a = b = c$. In terms of the *d* spacing directly, we get

$$d = \frac{a}{\sqrt{h^2 + k^2 + \ell^2}} \tag{21.8}$$

The Bragg equation for a cubic crystal is therefore (for the first-order diffraction, which is typically the strongest):

$$\lambda = 2\frac{a}{\sqrt{h^2 + k^2 + \ell^2}} \cdot \sin\theta \tag{21.9}$$

The angles of diffraction of (monochromatic) X rays by cubic crystals are thus relatively easily predicted, because the Miller indices themselves are restricted to whole numbers in cubic crystals. Depending on whether the crystal is simple cubic, face-centered cubic, or body-centered cubic, different planes are defined by the atoms in the crystal, and so different angles of diffraction may be possible. However, the pattern of possible angles is characteristic of the type of cubic crystal, because of the integral possible values of the Miller indices. Figure 21.24 shows the relative patterns of the diffracted X rays along with the Miller indices of the unit cell planes that diffracted the radiation.

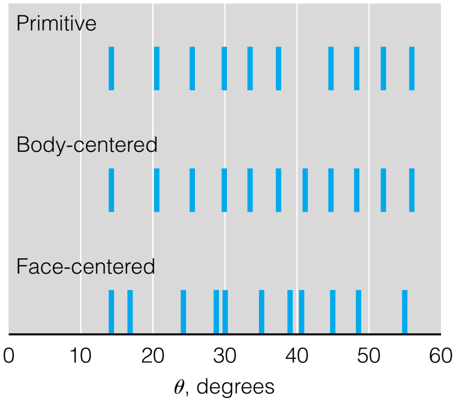


Figure 21.24 The pattern of diffracted X rays is characteristic of the type of unit cell a crystal has. Here, the patterns that the three cubic Bravais lattices cause on the X-ray diffraction is illustrated. For all three, we are assuming a unit cell parameter of 3.084 Å and an X-ray wavelength of 1.542 Å. Compare these patterns with the films in Figure 21.23: can you detect any correspondences between these two figures?

Because cubic crystals have such relatively simple X-ray diffractions, it is common to rewrite equation 21.8 in the forms

$$\sqrt{h^2 + k^2 + \ell^2} = \frac{a}{d} \quad \text{or} \quad h^2 + k^2 + \ell^2 = \frac{a^2}{d^2} \tag{21.10}$$

Because *h*, *k*, and ℓ are whole numbers, it is easy to construct a table of their possible values, and therefore the possible values of *a*/*d*. Crystals whose X-ray diffractions appear at these relative values are easily identified as cubic crystals. Table 21.3 shows such a table for comparative purposes. Because of occasional destructive interference due to diffracted X rays being exactly 180° out of phase, only certain combinations of *h*, *k*, and ℓ will appear depending on whether a crystal is primitive, face-centered, or body-centered cubic. The pattern of the possible Miller indices of refracting planes is therefore specific to

Table 21.3 Values of $(hk\ell)$ and $(h^2 + k^2 + \ell^2)$ that diffract X rays in cubic crystals[a]

$(hk\ell)$	$(h^2 + k^2 + \ell^2)$, sc	$(h^2 + k^2 + \ell^2)$, bcc	$(h^2 + k^2 + \ell^2)$, fcc
100	1	—	—
110	2	2	—
111	3	—	3
200	4	4	4
210	5	—	—
211	6	6	—
220	8	8	8
300, 221	9	—	—
310	10	10	—
311	11	—	11
222	12	12	12
320	13	—	—
321	14	14	—
400	16	16	16

Source: D. P. Shoemaker, C. W. Garland, and J. W. Nibler, *Experiments in Physical Chemistry*, 6th ed., McGraw-Hill, New York, 1996.)

[a] For each set of Miller indices, if the value $(h^2 + k^2 + \ell^2)$ is listed under each type of cubic cell, then that plane of atoms diffracts X rays. A — indicates that the plane does not diffract X rays (or experiences extinction). The pattern of diffracted X rays therefore indicates the type of cubic unit cell a crystal has.

the type of cubic unit cell a crystal has. (For additional details, consult a crystallography text.) Equation 21.10, Table 21.3, and Bragg's law are used together to determine the size and type of unit cell a cubic crystal has. The following example illustrates how to use these three items.

Example 21.9

An unknown crystal has some cubic unit cell. The refractions of X rays by a powdered sample are seen at the θ values of 13.7°, 15.9°, 22.8°, 27.0°, 28.3°, 33.2°, 36.6°, and 37.8°. If the X rays have a wavelength of 1.5418 Å, determine the following:

a. The d spacings for each refraction
b. The type of cubic unit cell
c. The unit cell parameter a (that is, the length of the cubic unit cell)

Solution

Table 21.3 indicates that only certain combinations of Miller indices are possible for diffracted X rays. We will perform the following steps:

1. Use Bragg's law to calculate a d spacing for each angle of diffraction.
2. Square the d spacing and determine its reciprocal. We now have $1/d^2$, but we still don't know a or the Miller indices.
3. Take the ratio of the two lowest reciprocals.
4. Look at the entries in Table 21.3. If the ratio is 0.5 (or $\frac{1}{2}$), it can be either primitive or body-centered cubic. To determine which it is, take the ratio of the seventh and eighth values of $1/d^2$. If the ratio is 0.875 (or $\frac{7}{8}$), it is body-centered cubic. If the ratio is 0.889 (or $\frac{8}{9}$), it is simple cubic.
5. If the ratio of the two lowest reciprocals is 0.75 (or $\frac{3}{4}$), the crystal is face-centered cubic.

a, b. To determine the crystal structure we construct the following table:

θ	*d* (from Bragg's law; Å)	$1/d^2$ (Å^{-2})
13.7	3.25	0.0947
15.9	2.81	0.127
22.8	1.99	0.253
27.0	1.70	0.346
28.3	1.63	0.376
33.2	1.41	0.503
36.6	1.29	0.601
37.8	1.26	0.630

Taking the ratio of the first two reciprocals:

$$\frac{0.0947}{0.127} = 0.746$$

which is close enough to 0.75: the crystal is face-centered cubic.

c. To determine the unit cell dimension, we can use equation 21.10:

$$(h^2 + k^2 + \ell^2) = \frac{a^2}{d^2}$$

Table 21.3 indicates that the first diffraction, occurring at 13.7°, must have the Miller indices (111). We therefore substitute, using the corresponding *d* spacing from the table above:

$$(1^2 + 1^2 + 1^2) = \frac{a^2}{(3.25\ \text{Å})^2}$$

Solving for the unit cell dimension:

$$a = 5.63\ \text{Å}$$

As it turns out, this is the unit cell parameter for sodium chloride, which has a face-centered cubic unit cell. This kind of procedure is applicable to any cubic crystal.

For other types of unit cells, the pattern of X-ray diffractions depends on the exact (nonperpendicular) angles that the unit cell's sides make with each other. A general discussion that is applicable to all such crystals is impossible because of this. However, there is still a relationship between the *d* spacings of the atomic planes and the Miller indices; it is just not as simple as for cubic cells. The equation relating the *d* spacing with Miller indices, unit cell dimensions, and unit cell angles is complex and will not be considered here.

Details of experimental X-ray crystallography can be obtained from texts on analytical chemistry or experimental physical chemistry.

Finally, we need to consider the fact that in an X-ray diffraction pattern, not all diffractions have the same intensity. (See Figure 21.23 as an example.) This might be considered unusual: the X rays going in have a given intensity; why is it that the X rays coming out have different intensities?

The answer lies in part with the atoms that are contributing to the individual diffractions. Not all atoms scatter X rays with the same efficiency. The ability of an atom to scatter X rays is directly related to the electron density of the atom. (It is this very concept that makes X rays useful for medical purposes: tissues composed of heavier materials, like bone, scatter X rays more than other tissues like organs, muscle, and skin. This allows us to use X-ray photographs to differentiate body tissues.) We can define a *scattering factor* f_A for atom A as a way to describe the ability of individual A atoms to scatter X rays. The higher the scattering factor, the better an atom scatters X rays, and so the stronger the final diffracted X ray. As you might expect, in general larger atoms have higher scattering factors than smaller atoms. Figure 21.25 shows diffraction patterns for NaCl and KCl—two very similar compounds but with ions of different sizes and, therefore, scattering factors. Although the diffractions show a similar scattering pattern, the intensities of similar diffractions are obviously different.

The intensity of a particular X-ray diffraction also depends partly on phase effects. Recall that electromagnetic radiation can constructively interfere or destructively interfere, as shown in Figure 21.16. For some crystals in which a diffraction from a plane of atoms is expected to occur, it turns out that diffraction from an adjacent plane contributes X rays *of the exact opposite phase:* the result is complete destructive interference, and the intensity of this expected diffraction is zero. This is the reason that odd values of the sum $h^2 + k^2 + \ell^2$ are absent for body-centered unit cells (see Table 21.3). For crystals that are composed of different atoms having similar scattering factors, there may be accidental destructive interferences that can dramatically reduce the intensity of an expected diffraction.

We finish this section on Miller indices by introducing a convenient use of Miller indices. We like to define a solid crystal as an infinite, regular array of atoms or molecules. In reality, however, we know that the array is not infinite; the crystal stops at some point. It stops at the surface of the crystal. In many cases, the *surface* of a crystal is not just some random arrangement of atoms or molecules making a microscopically rough boundary. For many crystals, over a large surface area (that is, on a scale of square nanometers or micrometers) the surface corresponds to a particular plane of atoms or molecules that can be described by a particular set of Miller indices. Figure 21.26

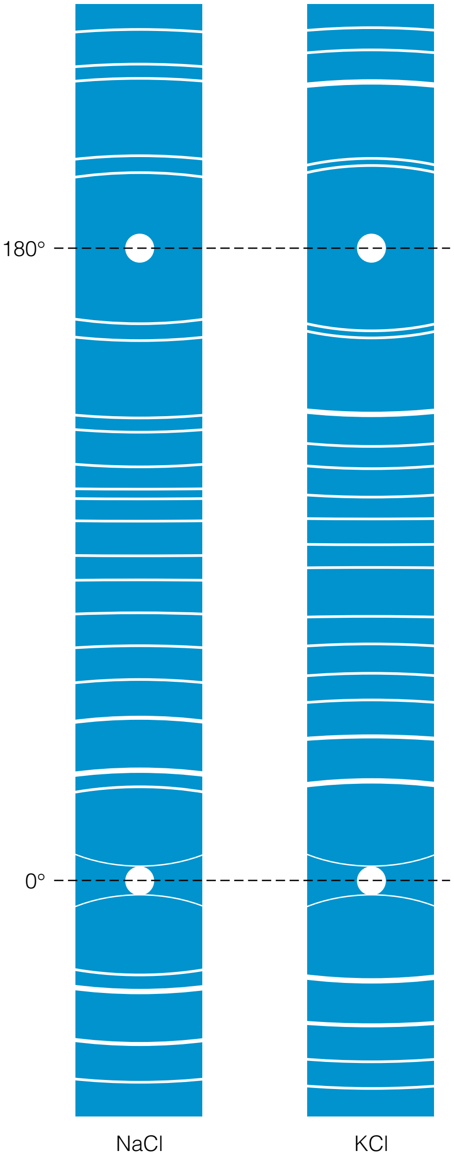


Figure 21.25 NaCl and KCl have the same unit cell, but the different sizes of the Na^+ and K^+ ions cause a different intensity of some individual diffractions.

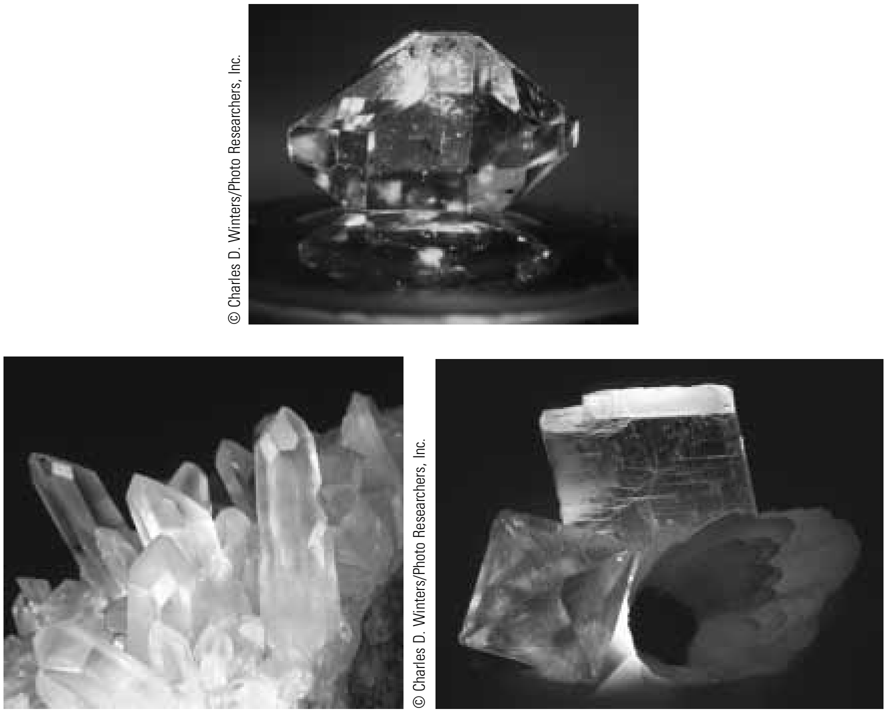


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Figure 21.26 Surfaces of crystals can also be described using Miller indices. In fact, the cutting and polishing of many gemstones follows specific Miller index planes. Mineralogists, gemologists, and lapidaries must know these planes in order to properly cut and polish gemstones.

shows examples of some crystalline surfaces. With care, large crystals with specific surface planes can be prepared, and the chemistry that occurs in the presence of each plane can be specific to that surface. We will consider surfaces in the next chapter, and Miller indices will reappear as a way to specify the arrangement of atoms on a surface.

21.7 Rationalizing Unit Cells

Why do crystalline solids have the unit cells that they do? There is actually some rationalization for the lattices that certain solid materials have.

We have already mentioned that many atomic elements, that is, elements whose molecules consist of individual atoms (like Ar and Fe), exist as either face-centered cubic or hexagonal closed-packed solids. (A substantial number of the remaining atomic elements are body-centered cubic.) Unit cells that are fcc or hcp represent the most efficient use of space: for solid-sphere atoms, about 74% of the available space is taken up by the solid spheres. The remainder, about 26%, is simply empty space. Such efficiency of packing was actually predicted by the astronomer Johannes Kepler in 1611.

Despite an unstated presumption, unit cells are not invariant for a given compound. Different unit cells may be preferred under different conditions of temperature and pressure. These are examples of *solid-solid phase changes.* The easiest illustrations are for elemental materials. Perhaps one of the best-known differences in unit cells is for elemental carbon, which has two common forms: graphite (a hexagonal unit cell, but *not* hcp) and diamond (face-centered cubic). Elemental iron, for example, is body-centered cubic below about 910°C, but between 910° and about 1400°C it becomes face-centered cubic. Metallic tin is tetragonal at room temperatures, but below about 13°C (which is not much below room temperature!) it adopts a cubic structure. This causes a major problem because in doing so, the unit cell increases in volume by over 20%. Temperature-dependent solid-state phase changes are a major engineering concern.

For molecular elements and compounds, the reasons for having a particular unit cell are complex and will not be considered. Generally, such materials adopt a unit cell that minimizes the overall energy of the compound. The choice of unit cell is therefore highly dependent on the molecule itself. There are also some marked solid-solid phase changes in molecular compounds. A well-known example is H_2O. Many unit cells are actually known for solid H_2O; that which we call “ice” is simply the stable crystalline phase at normal conditions of temperature and pressure. If the pressure were increased dramatically, the crystal structure of solid H_2O changes. Figure 21.27 shows a phase diagram of H_2O that illustrates the different crystal structures of H_2O.

Other molecular compounds can have equally complicated solid-state phase diagrams, and a discussion of molecular unit cells will not be pursued further here.

For simple ionic compounds, however, there are some guidelines. Ionic compounds are formed by the mutual attractions between cations and anions. The type of unit cell that is formed is strongly influenced by two factors: the relative sizes of the ions (which determine their ability to fill three-dimensional space), and the relative charges (which determine the relative number of cations and anions that are needed to have an overall electrically neutral compound). The concept of ionic size or *ionic radius* ultimately derives from crystallography. We cannot measure the size of an ion directly—indeed, quantum

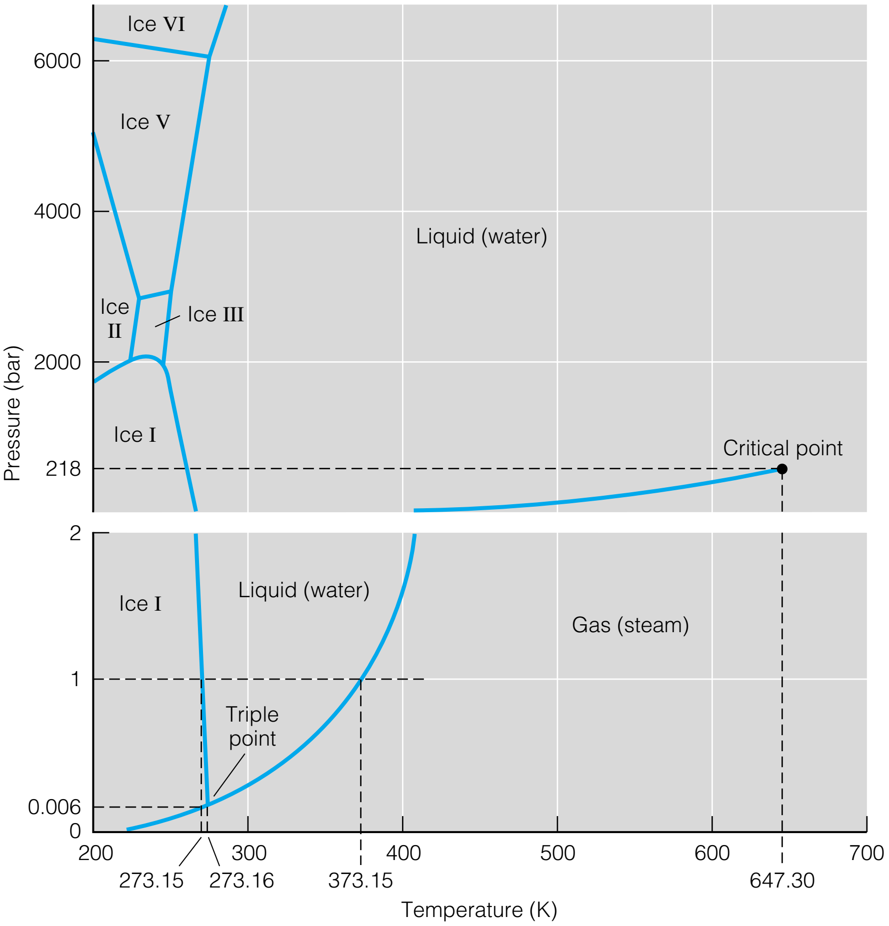


Figure 21.27 Phase diagrams can include different kinds of solid phase, as well as liquid and gas phase. H_2O, for example, has many different crystalline structures, depending on the temperature and the pressure. Each region represents a different solid phase of H_2O.

mechanics and its probabilistic interpretation of wavefunctions do not allow us to define a certain "size" for the electrons about an ion. But by measuring the crystalline parameters of unit cells of various crystals, we can determine a general size that an ion contributes to a crystal lattice and define that as the size (diameter or radius) of the ion. Table 21.4 lists the experimentally determined ionic radii for some ions. There are also several entries for polyatomic ions. Although it is not possible to assign a specific, single radius to polyatomic

Table 21.4 Crystalline ionic radii for various ions

Ion	Radius (Å)	Ion	Radius (Å)
Ag^+	1.26	K^+	1.33
Al^{3+}	0.51	Mg^{2+}	0.66
Au^{3+}	1.37	Na^+	0.97
Ba^{2+}	1.34	O^{2-}	1.31
Be^{2+}	0.35	Pb^{2+}	1.20
Br^-	1.96	S^{2-}	1.84
Ca^{2+}	0.99	Ti^{4+}	0.68
Cl^-	1.81	Zn^{2+}	0.74
Cr^{3+}	0.63	$NH_4{}^+$	1.48
Cs^+	1.67	$BF_4{}^-$	2.28
F^-	1.33	$SO_4{}^{2-}$	2.30
I^-	2.20		

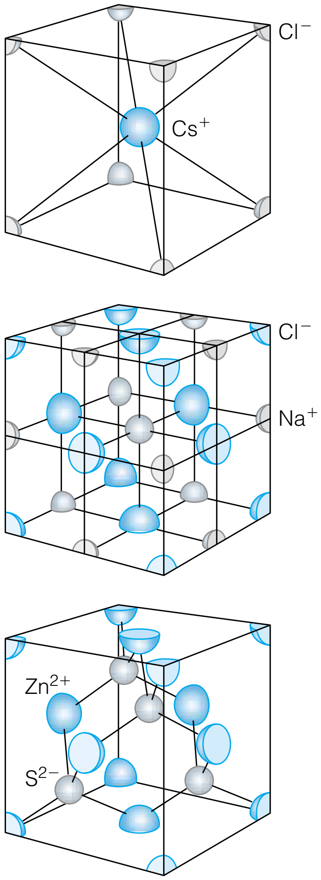


Figure 21.28 Typical unit cells for the cesium chloride, sodium chloride, and zincblende types of crystals.

ions, an "effective ionic radius" can be estimated from crystallography or energy determinations.

For ionic compounds that have a 1 : 1 stoichiometric ratio of cation to anion (like NaCl, CsCl, or MgO), the relative sizes of the ions determine whether the compound will have one of three possible unit cells. We use a label to define each type of unit cell. The following table summarizes this experimentally determined generality, in which the ratio in column 1 determines columns 2 and 3:

Radius ratio $\frac{r_{\text{smaller}}}{r_{\text{larger}}}$	Unit cell	Label
Greater than 0.73	Simple cubic	Cesium chloride structure
Between 0.73 and 0.41	Face-centered cubic	Sodium chloride structure
Less than 0.41	Face-centered cubic	Zincblende structure

Figure 21.28 shows typical unit cells for these 1 : 1 ionic crystals. The names of the unit cells are taken from common compounds that typify the general unit cell structure. "Zincblende" is a common name for zinc sulfide, ZnS, which typifies the unit cell structure.

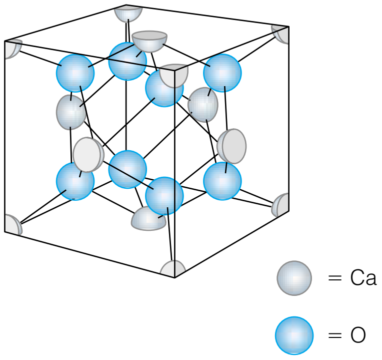
What's the difference between the sodium chloride and zincblende structure? They are both face-centered cubic structures, and they both have 1 : 1 ratios of ions in the ionic formula. But, as seen in Figure 21.28, the relative positions of the ions in the unit cell are different. In the sodium chloride structure, the ions not defining the unit cell (that is, not at the corners or in the faces) surround the unit cell–defining ions in the x, y, and z dimensions. If you were to extend the unit cell in any direction, you would find that each ion has six oppositely charged ions at equal distances from it. One way of stating this is that in the sodium chloride structure, each ion has a *coordination number* of 6.

However, in the zincblende structure, these other ions are in the body of the unit cell, and are not on axes that are perpendicular to each other. Although it might be harder to see, by extending the unit cell in any direction you can show that every ion has *four* oppositely charged ions the same distance away, making the shape of a tetrahedron about the original ion. In this case, the ions have a coordination number of 4.

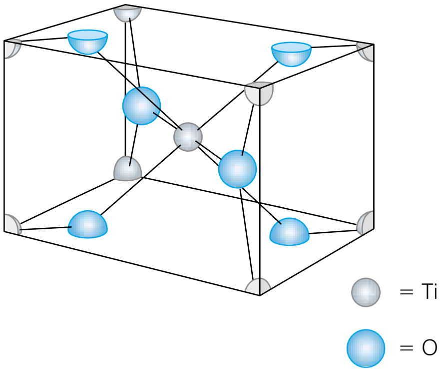
In either case, it is easy to show that the ratio of ions in the unit cell is 1 : 1. The two possible face-centered unit cells are consistent with a 1 : 1 ion ratio in the formula for the compound. The particular structure, however, depends on the relative sizes of the ions.

For ionic compounds that have a 1 : 2 or 2 : 1 ratio of cation to anion (like CaF_2 or K_2O), there are two common unit cell arrangements. Again, one can usually predict which arrangement a crystal has by considering the relative sizes of cation and anion. If the ratio $r_{\text{smaller}}/r_{\text{larger}}$ is greater than about 0.73, the unit cell is labeled the *fluorite structure* after CaF_2 (common name fluorite), which is shown in Figure 21.29a. If the ratio is less than 0.73, then the *rutile structure,* Figure 21.29b, is preferred. Rutile is a common name for TiO_2, which typifies the structure. Fluorite unit cells are face-centered cubic, whereas rutile is tetragonal (all 90° angles, but one unequal unit cell length).

One final note is that these predictions are generalities and do not hold for all crystals! The only certain way to know the crystal structure of a solid is from experiment. Example 21.10 illustrates some of the differences between prediction and reality.



CaF_2 (Fluorite)



TiO_2 (Rutile)

Figure 21.29 Typical unit cells for the fluorite and rutile types of crystals.

Example 21.10

Predict the structure(s) of the following crystals. Consult Table 21.4 for ionic radii when necessary.

a. Sodium sulfide, Na_2S
b. Lead, Pb
c. Magnesium, Mg
d. Silver bromide, AgBr
e. Ammonium chloride, NH_4Cl

Solution

a. From Table 21.4, Na^+ has a radius of 0.97 Å and S^{2-} has a radius of 1.84 Å. The ratio $r_{\text{smaller}}/r_{\text{larger}}$ is $0.97/1.84 = 0.527$, so we predict that this 2 : 1 ionic compound has a rutile structure. (It actually has a fluorite structure.)

b. Lead is a metallic element that is an atomic solid. We predict that it has one of the most efficient crystal arrangements, either face-centered cubic or hexagonal close-packed. (It has an fcc unit cell.)

c. Magnesium is also a metallic, atomic solid. Again, we predict either fcc or hcp. (Magnesium is hcp.)

d. From Table 21.4, we find that Ag^+ has an ionic radius of 1.26 Å and Br^- has a radius of 1.96 Å. The ratio $r_{\text{smaller}}/r_{\text{larger}}$ is $1.26/1.96 = 0.642$, suggesting a sodium chloride structure for this 1 : 1 salt. (AgBr does indeed have the sodium chloride crystal structure.)

e. Ammonium ions have an effective ionic radius of 1.48 Å, and Cl^- ions have a radius of 1.81 Å. The ratio $r_{\text{smaller}}/r_{\text{larger}}$ is 1.48/1.81, which equals 0.818. We predict a cesium chloride unit cell for ammonium chloride. (NH_4Cl has the cesium chloride unit cell.)

The above example shows that the generalities for predicting crystalline unit cells work but are not infallible. Again, the point should be made that experiment is the only way to know for certain what the unit cell of a crystal is.

21.8 Lattice Energies of Ionic Crystals

When ions of opposite charges come together to make a crystal, there is always a decrease in the overall energy. It is this decrease in energy that makes the crystal stable with respect to the individual, separated ions. It is also this decrease in energy that leads to the idea of the "energy" of an ionic bond.

The amount of energy given off when one formula unit of moles of ions come together from the gas phase to make a crystal is called the *lattice energy* or *lattice enthalpy* of the crystal. The second term reinforces the relationship to the enthalpy of the crystal formation process. For example, by definition, the lattice energy of sodium chloride, NaCl, is represented by the energy change of the molar reaction

$$Na^+\ (g) + Cl^-\ (g) \longrightarrow NaCl\ (s) \qquad \text{lattice energy} \equiv -\Delta_{\text{rxn}}H \qquad \textbf{(21.11)}$$

Notice that the lattice energy is defined as the *negative* of $\Delta_{\text{rxn}}H$. This is because it is understood that energy is always given off when separated ions come together to make ionic crystals. The lattice energy is therefore simply the absolute magnitude of that exothermic process. Table 21.5 lists some experimental lattice energies of some simple ionic crystals.

Table 21.5 Experimental lattice energies of some ionic crystals

Formula	Lattice energy (kJ/mol)	Formula	Lattice energy (kJ/mol)
LiF	1013	KCl	701
LiCl	834	KBr	671
LiBr	788	CsI	600
NaCl	769	CaF_2	2609
NaBr	732	$CaCl_2$	2223
Na_2O	2481	$CaSO_4$	2489
K_2O	2238	$SrSO_4$	2577
TiO_2	12150	$BaSO_4$	2469
K_2S	1979	Na_2SO_4	1827

The data in Table 21.5 suggest some simple trends. The higher the absolute charges on the ions, the higher the lattice energy. The larger the ion, the lower the lattice energy.

There must be some reason for these trends, especially considering the grand simplicity of the interaction of opposite charges. Coulomb's law states that the potential energy of two oppositely charged particles at a distance from each other is

$$E = \frac{q_+ \cdot q_-}{4\pi\epsilon_0 \cdot r} \tag{21.12}$$

where the absolute charges q_+ and q_- are expressed in units of coulombs (C), the distance r is expressed in units of meters (m), and ϵ_0 is the permittivity of free space. Note in equation 21.12 that the charge variables q_+ and q_- include the signs; that is, positive charges have a positive value of q_+ and negative charges have a negative value of q_-. Therefore, potential energies between opposite charges are negative (and therefore contribute to a lowering of energy), and potential energies between like charges are positive (therefore contributing to a raising of energy).

Given an understanding of Coulomb's law, it should be easy to calculate lattice energies given (1) the magnitude of the charge on the ions, and (2) their separation in the unit cell. It isn't that easy, though. Coulomb's law is a model for the ideal energy of interaction of two and only two charged bodies that interact at a given distance. An ionic crystal is a conglomerate of many, many ions that interact over a range of distances. The following example illustrates the difference between experimental values and the simple coulombic model.

Example 21.11

Sodium chloride, NaCl, has an experimental lattice energy of 769 kJ/mol. If the distance between Na^+ ions and Cl^- ions in crystalline NaCl is approximately 2.78 Å, what would Coulomb's law predict for the energy of interaction of 1 mole of sodium ions with 1 mole of chloride ions?

Solution

Both sodium and chloride ions have unit charges, but of opposite magnitudes. In units of coulombs, a unit charge is 1.602×10^{-19} C. For r = 2.78 Å or 2.78×10^{-10} m:

$$E = \frac{(+1.602 \times 10^{-19}\ \text{C})(-1.602 \times 10^{-19}\ \text{C})}{4\pi[8.854 \times 10^{-12}\ \text{C}^2/(\text{J}\cdot\text{m})](2.78 \times 10^{-10}\ \text{m})}$$

$$E = -8.297 \times 10^{-19}\ \text{J}$$

This is for a single pair of ions. For a mole of ions, we multiply this answer by Avogadro's number:

$$E \text{ (per mole)} = -4.995 \times 10^5 \text{ J/mol}$$

$$E = -499.5 \text{ kJ/mol}$$

This answer suggests that the lattice energy of NaCl should be about 499 kJ. The actual lattice energy is substantially higher than that, suggesting that the two-ion model is not very good.

In fact, the two-ion (perhaps more generally, the single-formula-unit) model is not very good because it ignores other surrounding ions. If you reconsider the diagram of the unit cell of NaCl in Figure 21.28, it should be clear why the two-ion model won't work: each ion is actually surrounded by *six* ions of the opposite charge! Shouldn't the model take this into consideration? But there's more: around each oppositely charged ion are six ions of the same charge as the central ion. These ions contribute a repulsive component to the overall ionic interactions and contribute to an *increase* in the total potential energy of the crystal. And around each of these like-charged ions are six oppositely charged ions, contributing to a decrease in the total energy, and around these . . . and so forth.

A proper model of lattice energy must take into account the layers of oppositely charged and like-charged ions that compose a crystal. The model also must take into account the repulsion between the electron clouds of all ions, no matter what the magnitude or sign of their charges. In fact, it is the balance between the attractions of opposite charges and the repulsions of electron clouds that dictates the size of the unit cells.

Without derivation (which can be found in crystallography texts), one expression for the lattice energy of an ionic crystal is

$$\text{lattice energy} = \frac{N_A \cdot M \cdot Z^2 \cdot e^2}{4\pi\epsilon_0 \cdot r}\left(1 - \frac{\rho}{r}\right) \qquad \textbf{(21.13)}$$

In the above equation, Z is the greatest common divisor of the magnitudes on the ions (that is, 1 for NaCl, Na_2O, and so on, and 2 for MgO, TiO_2, ZnS); e is the charge on the electron; r is the distance between oppositely charged ions (usually the closest or "nearest-neighbor" ions); and the $4\pi\epsilon_0$ term is the conversion between non-SI and SI units. N_A is Avogadro's number, so the lattice energy has units of joules per mole (meaning joules per mole of ionic crystal formula unit). There are two numerical parameters in equation 21.13: ρ and M. The *repulsive range parameter* ρ is a distance parameter that relates to the range of the repulsion between electron clouds. It is typically on the order of 0.1 times the value of r or less, showing that repulsive effects have a noticeable but small contribution to the lattice energy. The repulsive range parameter ρ has units of distance, typically Å.

The parameter M in equation 21.13 is called the *Madelung constant* for the crystal. The Madelung constant is the sum of the alternating coulombic attractions and repulsions of successive spheres of alternately charged ions about any single ion in an ionic crystal. These alternating attractions and repulsions depend on the arrangement of the ions in the crystal (which is ultimately determined from the crystal's unit cell) and the unit cell parameters (that is, the dimensional and angular parameters of the Bravais lattice). Because of this, you might think that it is easy to calculate the Madelung constant for a crystal. It's easy in theory, but not in practice. If you consider a simple system in which you recede from a central ion by moving through a series of nested spherical shells, the farther away you get from any one ion, the larger the number of ions in any spherical shell! The contribution of attraction or repulsion from each successive shell does not decrease very quickly.

Once the Madelung constant is determined from simple structural arguments, the lattice energy of an ionic crystal can be determined easily. These lattice energies can be used in cycles to evaluate energies of difficult-to-determine chemical processes. Such cycles are called *Born-Haber cycles.*

Table 21.6 lists some Madelung constants and repulsive range parameters ρ for various ionic compounds. Madelung constants are unitless, whereas repulsive range parameters have units of distance. Because Madelung constants can be determined from purely geometrical arguments, they are usually defined only for the crystal that typifies the unit cell (for example, any crystal that has the cesium chloride unit cell—simple cubic—has a Madelung constant of 1.7627). But because repulsive range parameters depend on the ion's charges as well as the unit cell dimensions, crystals having the same unit cell have different values for ρ.

Table 21.6 Madelung constants and repulsive range parameters of some ionic crystals

Formula	Madelung constant M	ρ (Å)
LiF		0.291
LiBr		0.330
NaCl	1.74756	0.321
NaBr		0.328
KCl		0.326
KBr		0.336
ZnS	1.6381	0.289
TiO_2	2.408	0.250
CsCl	1.7627	0.331

Example 21.12

Calculate the expected lattice energy of NaCl again, this time using equation 21.13 and using a Madelung constant of 1.748 and a repulsive factor of 0.321 Å. The distance between Na^+ ions and Cl^- ions is, again, 2.78 Å. Compare it to a lattice energy of 769 kJ/mol. Compare your answer with Example 21.11.

Solution

Recall that NaCl is a 1:1 ionic compound, so the greatest common divisor variable Z equals 1. If we want to use standard units at the outset, we should convert our 2.78 Å into meters to get 2.78×10^{-10} m. We will use

$$\text{lattice energy} = \frac{N_A \cdot M \cdot Z^2 \cdot e^2}{4\pi\epsilon_0 \cdot r}\left(1 - \frac{\rho}{r}\right)$$

and substitute for the various constants:

$$\text{lattice energy} = \frac{(6.02 \times 10^{23}/\text{mol})(1.748) \cdot 1^2(1.602 \times 10^{-19}\ \text{C})^2}{4\pi[8.854 \times 10^{-12}\ \text{C}^2/(\text{J}\cdot\text{m})](2.78 \times 10^{-10}\ \text{m})}\left(1 - \frac{0.321\ \text{Å}}{2.78\ \text{Å}}\right)$$

Note the slight inconsistency: in the second part of the equation, we still use r in units of angstroms. This is because the parameter ρ is given in units of Å, and to keep units consistent we keep the Å unit for r. As a ratio, it is required that the units cancel; we could just as easily convert ρ to units of meters. You should satisfy yourself that the units in the first part of the expression cancel appropriately to yield units of J/mol. Solving numerically:

$$\text{lattice energy} = 873{,}000\ \frac{\text{J}}{\text{mol}} \times 0.885$$

$$\text{lattice energy} = 773{,}000\ \frac{\text{J}}{\text{mol}} = 773\ \frac{\text{kJ}}{\text{mol}}$$

Compared to an experimental value of 769 kJ/mol, we find that equation 21.13 does a much better job of predicting lattice energies than Coulomb's law did.

Equation 21.13 is defined to give positive values for the lattice energy. It should be understood that when oppositely charged ions come together, total energy is always *decreased*. Therefore, the $\Delta_{rxn}H$ values of these processes are always negative, indicating an exothermic process.

21.9 Crystal Defects and Semiconductors

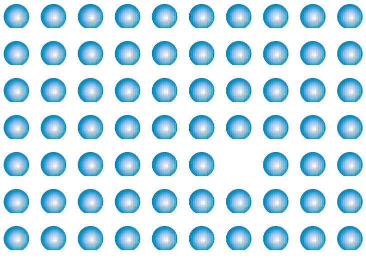
So far in this chapter, we have been working under the assumption that crystalline solids are perfect crystals. Every atom, ion, or molecule is assumed to be in exactly the right place in every unit cell throughout the entire solid crystal.

In reality, this is not the case. Most real crystals are full of imperfections. Even crystals that are considered very well ordered have an occasional lapse in crystal structure at the atomic and molecular level. These lapses are called *defects*.

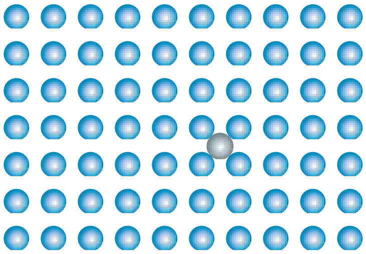
There are several different kinds of defects in crystals. Depending on the type and number of defects in any volume of crystal (that is, the type and density of defects), the physical and chemical properties of the crystal may be altered from the properties of the perfect crystalline form. Defects can be separated on the basis of whether they affect a single point, a line of points, or a plane of points. For simplicity's sake, we will assume that we are considering an atomic crystal, but all crystals—atomic, ionic, molecular—exhibit most of the defects discussed here.

The simplest point defect is when an atom is simply missing from its expected position. This type of defect is called a *lattice vacancy* (sometimes also called a *Schottky defect*). In another kind of defect, an additional atom is present. If the additional atom is crowded in with the rest of the atoms in the unit cell, then it must squeeze itself in between the normally occupied positions. This type of defect is called an *interstitial defect*. If, on the other hand, the additional atom is a chemically different atom that is taking the place of an atom of the normal unit cell, then it is considered a *substitutional defect*. Figure 21.30 shows a two-dimensional example of these three types of point defects in crystals.

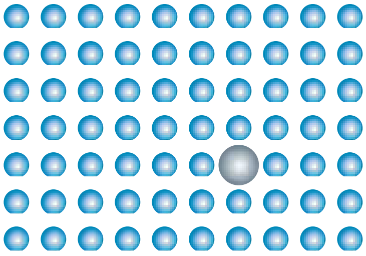
Line and plane defects are more complicated to illustrate. One type of line defect is found when a line of atoms or unit cells starts suddenly inside a crystal. Figure 21.31 shows a two-dimensional representation of this kind of line defect. Plane defects are usually seen at the surfaces of crystals or at interfaces between two smaller crystals in a larger piece of solid material, as seen in Figure 21.32. Plane defects can also exist between two different Bravais lattices of the same compound.



Lattice vacancy



Interstitial defect



Substitutional defect

Figure 21.30 Examples of the common types of defects in crystals. Even crystals that look very well ordered macroscopically may have a high density of such defects.

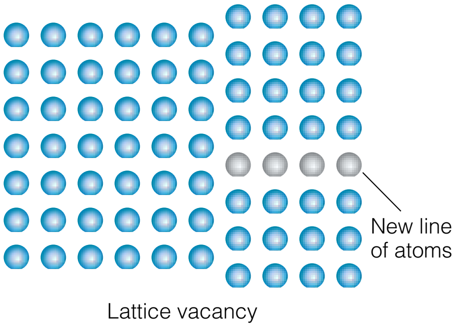


Figure 21.31 A line defect in a (two-dimensional) crystal.

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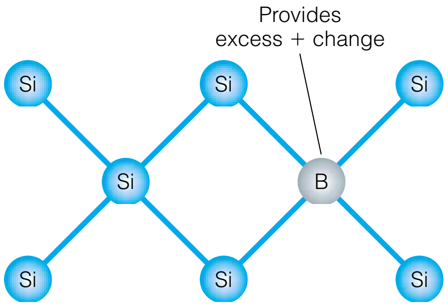
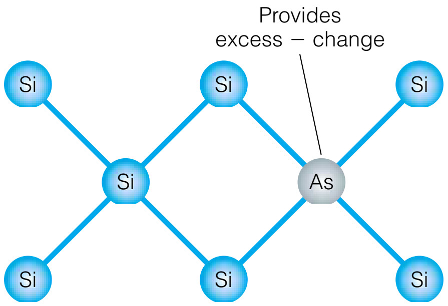
Figure 21.32 The surface that separates the two individual crystals can be considered a type of plane defect. In a perfect crystal, such an interface wouldn't exist.



(a) p-Type semiconductor



(b) n-Type semiconductor

Figure 21.33 (a) Substituting a boron atom for a silicon atom in crystalline Si reduces the number of electrons in the crystal by 1, making a positively charged "hole" and a so-called p-type semiconductor. Electrons can occupy these holes, allowing for electricity to conduct through the material. (b) Similarly, substituting an As atom introduces an extra electron, which is free to move through the solid. This is an n-type semiconductor.

The very word "defect" has negative connotations, but crystal defects are not necessarily bad. One area that takes advantage of crystal defects is semiconductors. For example, many semiconductors are composed mostly of silicon, whose crystal form is a covalent network solid. Pure silicon is actually nonconductive, but if a tiny percentage of substitutional defects is present, the conductivity properties of silicon are changed dramatically. For example, 10 parts per million of boron substituted in pure silicon increases the conductivity of the crystalline solid by a factor of 1000! A boron atom does this by substituting for a Si atom, but in doing so decreases the number of electrons in the solid by 1; see Figure 21.33a. The unpaired electron on the adjacent silicon atom is free to conduct electricity (but not very well; hence the *semi*conductor description of the doped silicon crystal). An equivalent way of stating this is that the boron atom "substitutes" a missing electron, called a *hole*, and it is the hole that conducts the electricity. (Although the definition of a hole relies on something that is *not* there rather than something that is, it is commonly invoked to discuss the conductivity of semiconductors. Electricity is conducted as electrons move to fill holes.) Semiconductors that are doped to decrease the number of electrons are called *p-type semiconductors*, the *p* standing for *positive*. That is, having fewer electrons implies a positive charge on a material. This is somewhat of a misnomer, because the crystal does *not* have a positive charge.

Similarly, substituting an atom that has more electrons than a Si atom does introduces additional electrons, as shown in Figure 21.33b. These excess electrons can also impart some conductivity to the Si crystal. Because of the additional electrons in the substitutional defect, these semiconductors are called *n-type semiconductors*, the *n* standing for *negative* using the reverse of the rationale for the p-type label.

Other substitutions (by different atoms and to different degrees) change the conductivity of silicon in other ways, and it is this variable conductivity that is the basis for all solid-state electronics. This intentional introduction of defects is called *doping*. In addition to silicon, other materials—properly doped—can be used as semiconductors. Some of these materials are 1 : 1 combinations of p^3 and p^5 valence shell atoms (Si has a p^4 valence shell, so on average the atoms have a silicon-like valence shell). GaAs and InAs are common materials that are also used for semiconductors.

21.10 Summary

In this chapter, we have seen how we can model the solid state of matter, assuming that the solid is well-ordered and composed of crystals. Not-well-ordered solids can be polycrystalline, or they may be amorphous. But the regularity of crystals helps us determine models for describing the solid phase.

Central to modeling the solid state is the understanding that there are only 14 basic crystal arrangements, called Bravais lattices. Crystals are ultimately composed of repeating units called unit cells, all having the same three-dimensional arrangement of atoms or molecules, all contributing to the entire crystal. A unit cell is to a crystal as an atom is to an element: it is the basic building block of the larger material. Also central is the idea that there is a simple mathematical model to determine how crystal lattices might interact with electromagnetic radiation, specifically X rays. The Bragg equation shows how we can relate the diffraction of X rays by a crystal to that crystal's structure. Crystals as simple as NaCl or as complicated as DNA can be studied using X-ray diffraction, and their structures deduced on the basis of their diffracting

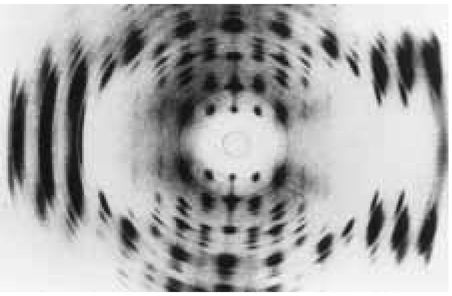


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Figure 21.34 Diffraction patterns from crystalline DNA were interpreted as DNA having a double-helix structure. The determination of the structure of DNA was a major development in biology.

behavior. In fact, one major success of X-ray diffraction techniques was the successful elucidation of the double-helix structure of DNA in the early 1950s (see Figure 21.34).

Because of the regularity of atoms and molecules in a crystal, many of the possible planes of atoms can diffract X rays. We use a system called Miller indices to label which plane of atoms is diffracting X rays, and different Bravais lattices have different planes, with characteristic Miller indices, that diffract. In this way, we can differentiate unit cells by their characteristic X-ray diffraction patterns. In the next chapter, we will find that Miller indices are also useful in describing the orientation of the surface of the crystal.

Unit cells of compounds are not always arbitrary. For many simple ionic compounds, the stoichiometry of the compound and the ion sizes contribute to a favored unit cell. We therefore have some ability to predict the expected unit cell of a compound. We can also calculate the bond energy of the ionic compound. Of course, the term bond energy is not strictly correct, since ionic crystals are held together by coulombic forces acting in three dimensions. The phrase lattice energy is more appropriate, since the bond energy is actually the energy released when oppositely charged ions attract each other to form a three-dimensional lattice. In determining a lattice energy, we must consider not just the attractions between oppositely charged ions, but the repulsions between like-charged ions as well.

Finally, we recognize that all crystals are not perfect. We can take advantage of imperfect crystals, including using some of them as semiconductors. Being able to take advantage of imperfect crystals depends, however, on an understanding of perfect crystals.

EXERCISES FOR CHAPTER 21

21.2 & 21.3 Types of Solids; Unit Cells

21.1. Give an atomic-level reason why ionic crystals are brittle.

21.2. Boron nitride, BN, is a very hard material, harder than diamond if prepared properly. Explain why it has diamond-like properties.

21.3. Explain how unit cells can be described for polycrystalline materials.

21.4. Figure 21.35 shows a unit cell of diamond. Identify the atoms that define the unit cell and determine the Bravais lattice of this structure of diamond. How many atoms are in the unit cell?

21.5. What is the relationship between the unit cell for diamond (Figure 21.35) and the unit cell for zincblende (Figure 21.28)?

21.6. How many different unit cells can a crystal have if the unit cell **(a)** has all 90° angles between its crystal axes; **(b)** has all of its unit cell dimensions the same length; **(c)** has at least one 90° angle between axes; **(d)** has no perpendicular axes or equivalent unit cell dimensions?

21.7. A researcher proposes an edge-centered cubic unit cell. What Bravais lattice would such a unit cell be better described as?

21.8. Use geometry and Figure 21.11 to show that in three dimensions the most efficient packing of hard-shell spherical atoms will take up about 74% of the space. Can you give a more exact figure for the amount of space taken up by the hard-shell spherical atoms?

21.9. Use geometry to determine the largest atom that will fit in a body-centered cubic unit cell. Express your answer in terms of the unit cell dimension a.

21.10. What is the maximum percentage volume that can be taken up by the atoms in a simple cubic unit cell? How much less is it than close packing?

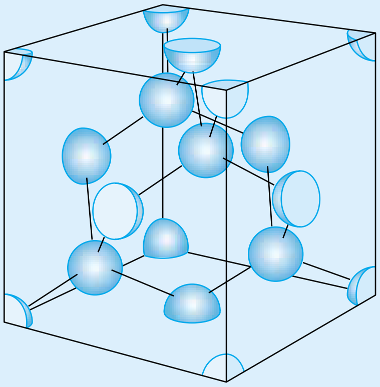


Figure 21.35 The unit cell of diamond. See exercise 21.4.

21.4 Densities

21.11. Prove the relationship in equation 21.3.

21.12. Zinc selenide, ZnSe, is a bright-orange compound that is sometimes used as a transparent window for infrared spectroscopy. It has a cubic unit cell with a = 5.669 Å and a density of 5.263 g/cm^3. How many ionic formula units of ZnSe are in each unit cell? Which cubic unit cell does it have?

21.13. Pyrite is a gold-colored mineral that is also known as fool's gold to miners. It is an ionic compound of iron and sulfur. It has a cubic unit cell with four formula units in the cell and a density of 5.012 g/cm^3. If the unit cell parameter is 5.418 Å, what is the formula of this material?

21.14. Talc is a complex silicate mineral having the formula $Mg_3Si_4O_{10}(OH)_2$. It has a monoclinic unit cell with cell parameters a = 5.287 Å, b = 9.158 Å, c = 18.95 Å, and β = 99.50°. If there are four formula units in the unit cell, determine the density of talc.

21.15. One form of quartz, SiO_2, has a hexagonal unit cell (three formula units per cell) with a = 4.914 Å and c = 5.405 Å. Determine the density of quartz.

21.16. Speculate on why the hexagonal unit cell is called "hexagonal" if the unit cell isn't a six-sided figure.

21.5 Determination of Crystal Structures

21.17. At least 43 of the elements that are composed of individual atoms (as opposed to diatomic gases, molecular elements like sulfur and phosphorus, covalent network elements like carbon, silicon, and germanium) have either hexagonal close-packed or face-centered cubic crystal lattices. How would you rationalize this?

21.18. Explain why zeroth-order X-ray diffraction does not depend on wavelength but all other orders of diffraction do. (Consider equation 21.5 and use n = 0.)

21.19. Use geometry to derive a form of Bragg's law in terms of the angle made with the *perpendicular* to the crystal plane, as opposed to the definition of θ shown in Figure 21.16.

21.20. Although first-order diffractions might occur at angles greater than 30°, if they do there will not be a second-order (or higher) diffraction. Use Bragg's law to argue why this is the case. (Consider the properties of the sine function at angles greater than 30°.)

21.21. Determine the angle of the first- and second-order diffractions of X rays having wavelength 1.5511 Å by a crystal of uranium dioxide, UO_2, if the d spacing is 5.47 Å.

21.22. Certain X rays generated by bombarding metallic copper have a wavelength of 1.54056 Å. Copper itself is face-centered cubic with a lattice parameter of 3.615 Å. At what angle does copper diffract its own X rays?

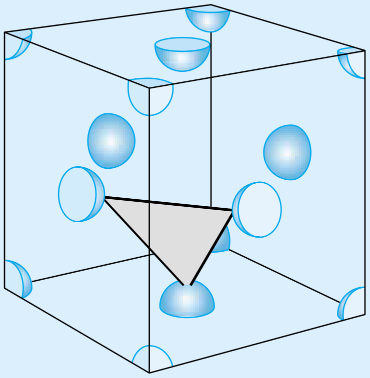


Figure 21.36 What are the Miller indices of the indicated plane? See exercise 21.26.

21.23. ^{56}Fe crystallizes in a body-centered unit cell having sides 2.8664 Å on a side. Its atomic mass is 55.9349 g/mol and its density is 7.8748 g/cm^3. From this information, calculate Avogadro's number, N_A. (This is one of the more accurate ways of determining N_A.)

21.6 Miller Indices

21.24. For a simple cubic lattice, what Miller indices describe the plane(s) that contain two of the three crystal axes?

21.25. For a simple cubic lattice, what is the ratio of the *d* spacings for the (100), (110), and (111) planes?

21.26. For a face-centered cubic lattice, what are the Miller indices of the plane made by the atoms centered in the faces of the unit cells as exemplified in Figure 21.36?

21.27. Because crystals exist in three dimensions, 3-D diagrams are often necessary to illustrate concepts. Using the single unit cell in Figure 21.21, draw a 2 × 2 × 2 set of eight cubic unit cells and draw the same plane in all unit cells.

21.28. Consider Figure 21.21. If the lower *right*most corner of the unit cell were selected arbitrarily as the origin, what would be the Miller indices of the indicated plane? Compare your answer to the solution of Example 21.7.

21.29. Any one plane can be described by more than one set of Miller indices, if negative indices are used. For a cubic unit cell the $(1\bar{1}1)$ plane is equivalent to what other plane whose indices are expressed in terms of all positive numbers? You may have to draw a few unit cells to determine an answer.

21.30. The aluminum-nickel alloy AlNi has a simple cubic lattice with a unit cell parameter of 2.88 Å. If X rays having a wavelength of 1.544 Å were used, at what angles would the X rays be diffracted by **(a)** the (100) plane of atoms; **(b)** the (110) plane of atoms; **(c)** the (210) plane of atoms?

21.31. A powdered sample diffracts X rays ($\lambda = 1.5418$ Å) at angles of 15.7°, 18.2°, 26.1°, 31.1°, and 32.6°. What type of cubic crystal is it, and what is the unit cell parameter?

21.32. Predict the angles of diffraction of X rays having $\lambda = 1.54056$ Å by KBr, which has the sodium chloride structure and a unit cell parameter of 6.59 Å. Consult Table 21.3.

21.33. Use geometric arguments to illustrate why the (111) plane of a body-centered cubic lattice does not cause detectable diffraction of X rays.

21.34. Explain why the X-ray diffraction pattern of CuZn, a 1:1 stoichiometric form of brass that has a body-centered cubic unit cell, is sometimes mistakenly interpreted as simple cubic. (Consider the scattering factors of the atoms.)

21.35. A given X-ray diffraction pattern is composed of diffractions that are roughly the same intensity. Explain whether or not this sole fact supports the possible identification of the sample as **(a)** KBr **(b)** CsF **(c)** NaCl **(d)** MgO.

21.7 Predicting Unit Cells

21.36. Predict the unit cells for the following materials: **(a)** potassium bromide, KBr; **(b)** cesium fluoride, CsF; **(c)** barium oxide, BaO.

21.37. Predict the unit cells for the following materials: **(a)** titanium sulfide, TiS_2; **(b)** barium fluoride, BaF_2; **(c)** potassium sulfate, K_2SO_4.

21.38. Sulfur, S, has some interesting solid-solid phase changes relatively close to room temperature. At room temperature it has an orthorhombic unit cell, but it is monoclinic at temperatures not much higher than boiling water. Why isn't elemental sulfur hcp or fcc?

21.39. Explain why the element carbon does not have a face-centered cubic or hexagonal close-packed unit cell even though we typically designate the element carbon with the monatomic formula C.

21.40. What is the coordination number in the cesium chloride cubic structure?

21.41. Determine the coordination number(s) of the ions in the fluorite and rutile unit cells. Why are there two unequal coordination numbers, whereas for cesium chloride, sodium chloride, and zincblende unit cells there is only one coordination number?

21.42. Which solid phase (that is, which allotrope) of carbon is more stable, graphite or diamond? (You should consult some of the tables in the thermodynamics section of this text.) Both solid phases exist under normal conditions of pressure and temperature. Explain why this is so, given that one solid phase is more thermodynamically stable than the other. Do their unit cells provide any suggestion for their relative stabilities?

21.8 & 21.9 Lattice Energies, Defects, and Semiconductors

21.43. Write the specific chemical reactions whose enthalpy change (or negative thereof) represent the lattice energy of **(a)** potassium fluoride, KF; **(b)** magnesium selenide, MgSe; **(c)** sodium oxide, Na_2O; **(d)** sodium peroxide, Na_2O_2.

21.44. Explain why lattice energy is considered a form of *potential* energy.

21.45. Write Born-Haber cycles showing the relationship between the formation reaction and the lattice energy definitions of each of the ionic compounds in exercise 21.43. You may need to review the definition of "formation reaction" from earlier in the text.

Table 21.7 Parameters for several unit cells[a]

Name	Lattice	*a*	*b*	*c*	α	β	γ
Coloradoite, HgTe	Cubic	6.46			90	90	90
Ice, H_2O	Hexagonal	4.5212		7.366			
Hafnia, HfO_2	Monoclinic	5.1156	5.17	5.2948		99.18	
Turquoise, $CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O$	Triclinic	7.424	7.62	9.910	68.61	69.71	65.08

[a] Lengths *a*, *b*, *c* are in units of Å. Angles α, β, γ are in degrees.

21.46. Compare the two-particle coulombic energy of attraction with the more precise calculation of the lattice energy for **(a)** cesium chloride, CsCl ($\rho = 0.331$ Å); **(b)** zincblende, ZnS ($\rho = 0.289$ Å); and **(c)** rutile, TiO_2 ($\rho = 0.250$). Are there any trends in the discrepancies? Use data from Tables 21.4 and 21.6.

21.47. The lattice energy for potassium iodide, KI, is 627.2 kJ/mol. If the ionic separation is 3.533 Å, what is the repulsive range parameter ρ for KI? You will have to determine which Madelung constant to use.

21.48. The concept of *charge density* involves the total charge of an ion divided by the space that the ion occupies. Using Table 21.5, determine a trend between charge density of an ion and the lattice energy of similar ionic crystals. Can you justify this trend on physical principles?

21.49. Lattice energies can also be defined for atomic elements like the gases He, Ne, and Ar. **(a)** Explain why equation 21.13 is not applicable to such crystals. **(b)** How would a scientist measure the lattice energy of He, Ne, Ar, and so on? Consider Chapters 1–8 in developing your answer.

21.50. Studies of crystals of He, Ne, Ar, and so on must be performed in vacuum systems that have an apparatus that can reach low temperatures so these elements are solids. These vacuum systems should not have hydrocarbons in them that might decompose to give off H atoms or H_2 molecules into the vacuum system. Why?

21.51. Solid palladium metal is known to actually absorb hydrogen gas, and no other. This behavior is used to make ultra, ultra-pure hydrogen. (In fact, because of this, hydrogen can be obtained in purer form than any other element.) What kind of defect are the hydrogen molecules probably making in the solid Pd metal? On the basis of your answer, can you rationalize why hydrogen is absorbed by Pd and no other gas?

21.52. Gallium arsenide (GaAs) can also serve as a basis for a semiconductor. It has a structure similar to that of elemental silicon, but with alternating gallium and arsenic atoms. Draw an electron-dot type of diagram of a unit cell of GaAs as well as n-type and p-type substitutions for a semiconducting material based on GaAs. What can be substituted for Ga for each type of semiconductor? What can be substituted for As for each type of semiconductor?

21.53. Suggest dopants for GaAs that would yield **(a)** a p-type semiconductor, and **(b)** an n-type semiconductor.

21.54. Explain how holes conduct electricity.

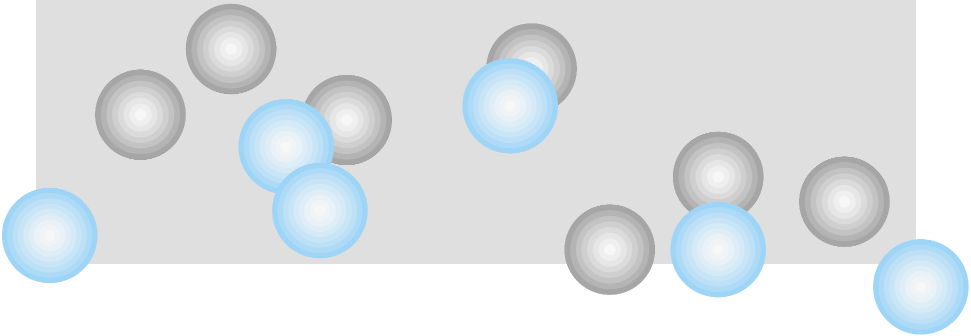
Symbolic Math Exercises

21.55. Calculate the volume of the unit cells for the compounds in Table 21.7.

21.56. Set up a program or formula to calculate the angles of diffraction for a cubic crystal in terms of the *h*, *k*, and ℓ values. **(a)** Calculate these angles for incoming X radiation of 1.5418 Å and a simple cubic lattice having a lattice parameter of 6.46 Å. **(b)** Use Table 21.3 to determine which diffractions would be absent if the crystal were body-centered cubic or face-centered cubic.

22

Surfaces



THE READER MIGHT WONDER WHY an entire chapter is devoted to surfaces. After all, they seem fairly easy to understand: the physical boundary of any condensed-phase object is called a *surface,* and there doesn't seem to be anything special about them. The top of a desk, the blacktop of a road, are surfaces that we encounter daily, and there does not seem to be any unusual behavior associated with them.

Perhaps on a mundane level this is true. But now that we understand that matter is composed of atoms, that these atoms behave according to the laws of thermodynamics and quantum mechanics, and that gas and solid phases themselves behave in some understandable fashion, we should be willing to think that surfaces are worthy of special attention. A surface represents a series of points making a plane where one material ends and another begins. This discontinuity of matter means that the bulk properties of the material will not necessarily be found at the surface. In order to understand how surface properties differ from bulk properties, we need to consider some of the ways surfaces are defined and how they are different from the bulk material.

Therefore, we conclude our presentation of physical chemistry by considering surfaces. This topic has been placed at the end of the book because many of the ideas considered in previous chapters are applied here: thermodynamics, quantum mechanics, kinetics, and the structure of the solid state. Rather than consider the physical chemistry of surfaces in different chapters as some texts do, we present it a single chapter and see how the models of physical chemistry can be used to understand the behavior of surfaces.

22.1 Synopsis

Surfaces are everywhere, but (or because of this) they are easily ignored. However, they have a major impact on our understanding of matter and how matter interacts.

There are several ways we can consider surfaces. First, we can think of a surface as a thin film, one atom or molecule thick. Second, we can consider a surface as an interface between two different materials, like the boundary between two immiscible liquids or between a liquid and a gas or a vacuum, or a solid and a gas, a liquid, or a vacuum. Third, we can consider surfaces as terminations of solid crystals, an idea that was mentioned briefly in the previous chapter.

Surfaces have properties that are different from bulk materials. Why? At any boundary between two materials, there is an imbalance of interactions that ultimately affects the properties of the boundary. This is what we will find with surfaces. There is a property called surface tension that has no bulk equivalent, yet it can have a major influence on the behavior of liquids. We experience those influences every day with water. Interfaces, which are boundaries between phases, have properties that are dictated by surface effects. Curved surfaces, like those of liquid droplets, also have unique properties. These will be explored briefly.

Surfaces of crystalline solids can be specifically defined, thanks to the fact that planes of atoms in crystals can be specifically defined. Some of the ideas from the previous chapter on crystals will be applied here. Finally, we recognize the fact that the presence of certain surfaces speeds up, or catalyzes, some chemical reactions. Again, why? It turns out that there can be an interaction between the reactants and the surface itself that decreases the activation energy of the reaction, and therefore speeds up the rate. Catalysis of chemical reactions is an important industrial concern because in industry time is money. The physical chemistry of surfaces provides the basis for understanding why catalysis by surfaces occurs.

22.2 Liquids: Surface Tension

Under some circumstances, a material can spread out into a monatomic or monomolecular layer or *film.* For example, solutions of stearic or oleic acid (both long-chain fatty acids) in a hydrocarbon solvent can be carefully dripped onto water; when the solvent evaporates, the remaining fatty acids can arrange themselves into a monomolecular film on the water's surface. Such films have a definite surface coverage (that is, a definite area) depending on the number of fatty acid molecules present.

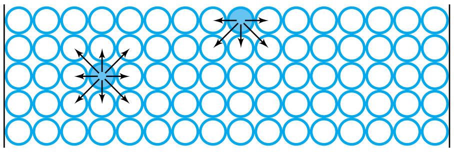


Figure 22.1 The atoms or molecules at the surface of a liquid can be considered a film. First consider the liquid particle in color at the lower left, below the surface. It interacts with other liquid particles all around it, with an overall balance of forces. However, a similar particle at the surface has interactions only down and to the sides. With no liquid particles above the surface layer, an imbalance of forces occurs that is the ultimate cause of surface effects.

However, the surface layer of atoms/molecules of a liquid can also be considered such a film, shown diagramatically in Figure 22.1. Further, we might suggest that this surface layer would have different properties than the bulk material. This is because the surface layer isn't really "bulk." Bulk atoms or molecules are surrounded on all sides by other molecules of the same material. At the surface, atoms or molecules are surrounded by the same molecules on one side but *different* molecules (or nothing) on the other. Forces between different materials (or between one material and nothing) are different, implying that the forces on the single surface layer of molecules are different from those in the bulk. Therefore, surface molecules aren't really bulk species and their behavior might not be the same as the bulk material.

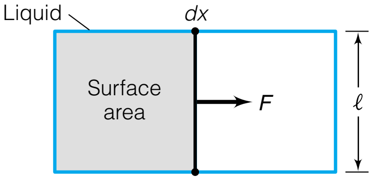


Figure 22.2 The experimental setup to define the surface tension γ. See text for discussion.

Suppose we want to increase or decrease the amount of surface available, perhaps by changing the shape of the liquid so that more surface area is exposed. Because of the differing forces acting at the surface, it will require work to change the surface area. Figure 22.2 shows a diagram of what we are trying to accomplish for an idealized system. If we want to increase the size of the rectangular surface area, then we have to do work *on* the liquid and against the unbalanced forces that exist at the surface. (Again, increasing surface area of a liquid requires that work be done *on* the liquid. Conversely, if the surface area is decreased, work is done *by* the liquid on the surroundings.) If the magni-

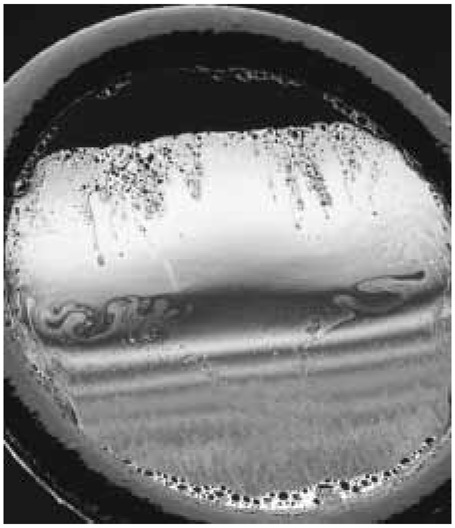


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Figure 22.3 A film has two surfaces and so requires twice the force to increase its size.

tude of the unbalanced force is represented by F, then the infinitesimal amount of work needed to increase the rectangular area by moving one boundary out by an infinitesimal amount dx is

$$dw = +\, F \cdot dx \tag{22.1}$$

The + sign is written explicitly to emphasize that this is work done *on* the liquid. This equation is the exact analogy of the physical definition of work (that is, work equals force times distance). If we refer to the illustration in Figure 22.2, the rectangle has a width labeled ℓ. We can define the (unbalanced) force per unit distance, or F/ℓ, as the variable γ, so that equation 22.1 becomes

$$dw = +\, \gamma \cdot \ell \cdot dx$$

The product of the width ℓ and the infinitesimal distance dx equals the infinitesimal change in area, dA, of the surface. The above equation becomes

$$dw = +\, \gamma \cdot dA \tag{22.2}$$

The variable γ is called the *surface tension* of the liquid.

If the system illustrated in Figure 22.2 were collapsed so that it were a film of material rather than a bulk liquid, then the work would be twice the amount predicted from equation 22.2: there are now two surfaces, not one. Figure 22.3 shows a picture of a film in which the work would be twice what equation 22.2 calculates. In this case, the surface tension γ would be defined as

$$\gamma = \frac{F_{\text{film}}}{2\ell} \tag{22.3}$$

where the factor of 2 in the denominator is there because we want to consider surface tension as a force per length *per surface*. In this case, F_{film}—the unbalanced force experienced by the surfaces of the film—is twice the force for a single surface, so in either case γ has the same value. Table 22.1 lists surface tensions of some common liquids. Surface tension has units of force per

Table 22.1 Surface tensions of various liquids

Liquid	Temperature (°C)	Surface tension, γ (dyn/cm or erg/cm^2)[a]
Acetic acid	20	27.8
Acetone	20	23.7
Bromine	20	41.5
Chloroform	20	27.1
Diethyl ether	20	17.0
Ethanol	20	22.8
Ethyl ether	50	13.5
Glycerine	20	63.4
Helium	−270	0.24
Mercury	25	485.5
Water	0	75.6
Water	10	74.22
Water	20	72.75
Water	60	66.18
Water	100	58.9

Source: D. R. Lide, ed., *CRC Handbook of Chemistry and Physics,* 82nd ed., CRC Press, Boca Raton, Fla.

[a] To convert to units of J/m^2, multiply by 1×10^{-3}.

distance or energy per area, and can be expressed in N/m, dyn/cm, erg/cm^2, or J/m^2.*

Surface tension is a characteristic of a liquid that varies with temperature, as might be expected. At the critical temperature—the temperature at which the distinction between liquid and gas phases disappear—the surface tension goes to zero.

Because work is done when changing the area of a surface, we should be able to correlate this work to one of the thermodynamic state functions. Recall that we found in an earlier chapter that the Gibbs energy is equal to the maximum amount of non-pV work that a process could do. Since changing the area of a surface is not pressure-volume work (just like electrical work isn't pressure-volume work), then "surface-tension–area" work must be related to the Gibbs energy. For a reversible change in surface area that occurs at constant temperature and pressure, we have

$$dw = dG = \gamma \cdot dA \tag{22.4}$$

This equation implies three things. First, we can integrate equation 22.4 to get

$$w = \Delta G = \gamma \cdot \Delta A \tag{22.5}$$

Second, we can rearrange equation 22.4 to solve for the surface tension in terms of a partial derivative at constant temperature and pressure:

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,p} \tag{22.6}$$

Third, if we want to consider the natural variable equation for dG for a liquid system whose surface area is changing, we must include the change in the Gibbs energy due to surface area change:

$$dG = -S\,dT + V\,dp + \gamma\,dA \tag{22.7}$$

The surface tension is sometimes also referred to as the *Gibbs surface energy* of a condensed phase. It is understood that it is a Gibbs energy per unit area, since this is consistent with the units used to define γ.

Example 22.1

How much work is required to increase the surface area of a container of water from 200.0 cm^2 to 300.0 cm^2? Such work might have to be performed on the water if, for example, a plastic container deforms and exposes a larger surface area. The surface tension of water is 72.75 erg/cm^2 at 20°C.

Solution

Using the integrated expression in equation 22.5, we figure that the change in area, ΔA, is $(300.0 - 200.0)$ cm^2 or 100.0 cm^2. Using equation 22.5:

$$w = \gamma \cdot \Delta A = \left(72.75\,\frac{\text{erg}}{\text{cm}^2}\right) \cdot 100.0\ \text{cm}^2$$

or, simply,

$$w = 7275\ \text{erg}$$

---

*A dyne (abbreviation dyn) is the unit of force in the cgs system of units, and is commonly used to express surface tensions. 1 N = 100,000 dyn.

Since an erg equals 1×10^{-7} joules, this work is equal to 0.0007275 J. This is not a lot of work in an absolute sense, but in a relative sense it does have an effect on the mechanical properties of the liquid (which we will consider later).

Example 22.2

In a zero-gravity environment, a sample of mercury has a spherical shape. Consider a sample that has a 1.000-cm radius. Determine how much work must be performed to separate the mercury into 10 equal spheres, assuming that the only work done is related to the change in surface energy. Recall that the surface area of a sphere is $4\pi r^2$ and its volume is $\frac{4}{3}\pi r^3$. The surface tension of mercury is 435.5 erg/cm^2.

Solution

If the only work that needs to be performed is related to the changing surface area of the drops, then we need to calculate the ΔA value for going from one 1.000-cm drop to 10 equal-volume drops. The single 1.000-cm-radius drop has a surface area of

$$A = 4\pi r^2 = 4\pi(1.000\ \text{cm})^2 = 12.57\ \text{cm}^2$$

Its volume is

$$V = \tfrac{4}{3}\pi r^3 = \tfrac{4}{3}\pi(1.000\ \text{cm})^3 = 4.189\ \text{cm}^3$$

If 10 equal drops of mercury were formed, then each drop should have a volume of $\frac{4.189}{10}$ or 0.4189 cm^3. Using the volume equation, we can determine the radius of a drop having that volume, and then determine its surface area:

$$0.4189\ \text{cm}^3 = \tfrac{4}{3}\pi r^3$$

$$r = 0.4642\ \text{cm}$$

and so the surface area of a smaller drop is

$$A = 4\pi r^2 = 4\pi(0.4642\ \text{cm})^2 = 2.708\ \text{cm}^2$$

If there are 10 drops of the same size, then the total area is $10 \times 2.708\ \text{cm}^2 = 27.08\ \text{cm}^2$. The change in area for the process is therefore

$$\Delta A = (27.08 - 12.57)\ \text{cm}^2 = 14.51\ \text{cm}^2$$

Again, using the integrated equation 22.5, we find the work as follows:

$$w = \gamma \cdot \Delta A = \left(435.5\ \frac{\text{erg}}{\text{cm}^2}\right) \cdot 14.51\ \text{cm}^2$$

$$w = 6319\ \text{erg} = 6.319 \times 10^{-4}\ \text{J}$$

Again, this example shows that only a small amount of work is needed, but it does suggest that work is needed to turn large drops of liquid into an equal mass of smaller drops of liquid. The reverse argument is that smaller drops of liquids will turn into the same mass of a *smaller* number of *larger* droplets, and in doing so work/energy will come *out* of the system. Since going to a lower energy is usually (but not always) an indication of a preferred, spontaneous process, the above example suggests that material will prefer—from an energy perspective—to be in the form of one body rather than multiple smaller bodies. This is indeed the case.

The relationship of surface tension to free energy also explains another phenomenon. According to equation 22.5,

$$\Delta G = \gamma \cdot \Delta A$$

In words, this equation says that the change in the Gibbs energy is directly proportional to the change in area of a liquid. If we consider an isothermal, isobaric process (that is, $dp = 0$ and $dT = 0$; these conditions are necessary when you consider the natural variable expression in equation 22.7), the process is spontaneous if ΔG is negative. Since surface tension must be a positive number, this implies that ΔA for a spontaneous process must be negative: a spontaneous process must occur with a corresponding *decrease* in surface area.

It has long been known that a sphere is the most compact solid object: it has the minimum surface area for any given volume. Therefore, the effects of surface tension require that *liquids assume a spherical shape if no additional forces are acting on them.* In the absence of gravity, this is indeed what happens (see Figure 22.4), and it is ultimately caused by the surface tension of the liquid. In many instances, liquid amounts are large enough that effects due to gravity distort the ideal spherical shape of liquids. However, for small amounts—like small drops of water on a plastic surface—the tendency toward a spherical shape can be obvious. Figure 22.5 shows an example of a phenomenon that is probably familiar—and whose ultimate origin is surface tension.

Finally, surface tension explains why certain phenomena occur, like insects walking on water or a needle or razor blade floating on water. It takes work—energy—to change the area of a surface; it takes work—energy—to pass *through* a surface. (In passing through a surface, distortion of the surface must occur.) If a process occurs without enough work to overcome the surface tension, the process will not break the surface. Insects typically experience a very tiny area of contact with a surface, so they float on water. Needles and razor blades can be placed so lightly that the force due to their gravity does not overcome the surface tension, so that they too will float on water.


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Figure 22.4 Because of surface tension effects, liquid droplets that do not experience other effects adopt a spherical shape.

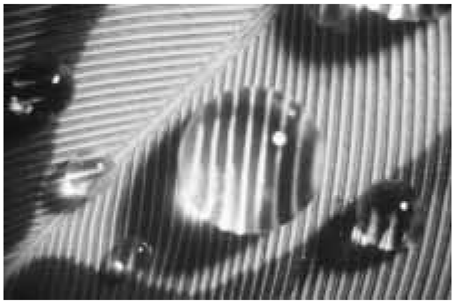
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Figure 22.5 Even though the effects of gravity can alter the ideal shape of liquid droplets, the tendency of small liquid droplets toward a spherical shape is obvious. This tendency is caused by surface tension.

Example 22.3

Show that a razor blade can float on water (which can be demonstrated experimentally if the system is set up carefully enough). Do this by calculating the work needed to move a razor blade by a distance equal to its thickness, and comparing it to the work needed to increase the surface area of water by the area of the razor blade. A typical double-edged razor blade has dimensions of 19.9 mm by 38.9 mm, a thickness of 0.250 mm, and a mass of 1.1240 g (and therefore experiences a gravitational force of 1.1462×10^{-4} N). Water has a surface tension of 72.75 erg/cm^2. Ignore buoyancy effects and other interactions (although in reality they can have a significant impact).

Solution

We need to show that to make a "hole" in the surface of the water large enough to pass the razor blade through requires more energy than is generated by moving the razor blade down by a distance of one thickness. First, we will calculate the decrease in gravitational potential energy as a 1.1240-g razor blade moves down 0.250 mm. To do this, we use the classical physics definition of work, force times distance:

$$\text{work} = \text{force} \times \text{distance}$$

$$\text{work} = (1.1462 \times 10^{-4}\ \text{N}) \times (0.250\ \text{mm}) \times \frac{1\ \text{m}}{1000\ \text{mm}} = 2.87 \times 10^{-8}\ \text{J}$$

Therefore, we will get 2.87×10^{-8} J of gravitational work out of the system as the razor blade drops 0.250 mm. Is this enough to overcome the energy required to pass through the water's surface? In order to do so, the razor blade must make a "hole" 19.9 mm by 38.9 mm large, or

$$\text{area} = 19.9\ \text{mm} \times 38.9\ \text{mm} \times \left(\frac{1\ \text{cm}}{10\ \text{mm}}\right)^2$$

$$\text{area} = 7.74\ \text{cm}^2$$

Given a surface tension of 72.75 erg/cm^2, we can calculate the energy needed to increase the area of the water by that much:

$$\text{energy} = \left(72.75\ \frac{\text{erg}}{\text{cm}^2}\right) \times (7.74\ \text{cm}^2) \times \frac{1\ \text{J}}{1 \times 10^7\ \text{erg}}$$

We are including the conversion from erg to joule. The energy needed to increase the water's area is

$$\text{energy} = 5.63 \times 10^{-5}\ \text{J}$$

This is several orders of magnitude more energy than is given off by the razor blade dropping through the surface. This suggests that a razor blade will, indeed, float on the surface of water.

22.3 Interface Effects

In the previous section, we showed that the surface tension was related to some thermodynamic functions, namely work and the Gibbs energy. What other thermodynamic manifestations are there for liquid surfaces? Several of these manifestations involve the interactions of two (or more) phases at their surfaces.

One thermodynamic variable, pressure, shows some unusual effects due to the presence of a surface. Consider a liquid in contact with another phase, like another liquid or even a gas or vacuum. Let us define region I as the liquid, and region II as the other phase in contact with the liquid. Together, these two regions represent our system, to be considered thermodynamically.

If the combination of these two regions is considered an isolated system at equilibrium, then the overall change in energy of the system, dU, is zero. (This is directly from the first law of thermodynamics.) We can define $dU[_I$ *as the change in internal energy of region I and*] dU_{II} as the change in internal energy of region II. But there is also a surface energy due to surface tension at the boundary between the two regions. This boundary is called the *interface*. Although we previously considered surface tension's relationship to the Gibbs free energy, the surface-tension–area work is also equal to the change in internal energy as long as other thermodynamic variables (S and V, the natural variables of internal energy) are kept constant:

$$dU_\sigma = \gamma \cdot dA \tag{22.8}$$

where dU_σ represents an interfacial internal energy.

From first law considerations, as mentioned earlier,

$$dU = 0$$

for this system. But when we separate the system into subsystems, each of which has its own internal energy, we can include the surface energy. We have

$$dU = dU_{\mathrm{I}} + dU_{\mathrm{II}} + dU_{\sigma} = 0 \tag{22.9}$$

Note something very interesting about this equation. It requires that the *total* internal energy, dU, be zero; it does not require that dU for either region, or for the interface, be unchanging. By defining a natural variable expression for each region and using the dU_{σ} value for the interface (equation 22.8), we can rewrite equation 22.9 as

$$(T_{\mathrm{I}} \cdot dS_{\mathrm{I}} - p_{\mathrm{I}} \cdot dV_{\mathrm{I}}) + (T_{\mathrm{II}} \cdot dS_{\mathrm{II}} - p_{\mathrm{II}} \cdot dV_{\mathrm{II}}) + (\gamma \cdot dA) = 0$$

We will leave out the explicit multiplication signs in the next few equations. To simplify the above expression, we note that the temperatures of each region must be equal (that is, T_{I} equals T_{II}), and that any infinitesimal entropy change by one region ought to be balanced by an equal and opposite infinitesimal entropy change by the other region. (This is the same thing as saying that $dS = 0$ for the entire system under these conditions.) Mathematically, then, the $T\, dS$ terms cancel. What is left, after rearranging, is

$$\gamma\, dA - p_{\mathrm{I}}\, dV_{\mathrm{I}} - p_{\mathrm{II}}\, dV_{\mathrm{II}} = 0 \tag{22.10}$$

Notice that we are *not* assuming that the pressures in each region are the same! This is a key point. We will note, however, that if the volume of region I changes, then the volume of region II must change by the same amount but in the opposite direction. That is, as one region grows, the other gets smaller, and by equal magnitudes (and vice versa, but always by equal magnitudes). The mathematical way of expressing this is

$$dV_{\mathrm{I}} = -dV_{\mathrm{II}} \tag{22.11}$$

Since we are interested in region I (the liquid), we will substitute for dV_{II} to eliminate it. Equation 22.10 becomes

$$\gamma\, dA - p_{\mathrm{I}}\, dV_{\mathrm{I}} + p_{\mathrm{II}}\, dV_{\mathrm{I}} = 0$$

and, after rearranging terms,

$$\gamma\, dA + (p_{\mathrm{II}} - p_{\mathrm{I}})dV_{\mathrm{I}} = 0 \tag{22.12}$$

In equation 22.12, we have factored out the dV_{I} variable from two of the terms. Equation 22.12 is interesting because we have not presumed that the pressures in the two regions are equal, and in doing so have derived an equation that relates their difference with the surface tension! We can algebraically rearrange equation 22.12 to get

$$(p_{\mathrm{I}} - p_{\mathrm{II}})\, dV_{\mathrm{I}} = \gamma\, dA$$

(Notice how the two pressures have switched their relative orders, because of the algebra.) We can combine the two differentials to get

$$(p_{\mathrm{I}} - p_{\mathrm{II}}) = \gamma\left(\frac{\partial A}{\partial V_{\mathrm{I}}}\right) \tag{22.13}$$

which relates the pressure difference on either side of an interface with the surface tension and how the area of the liquid changes with volume. Equation

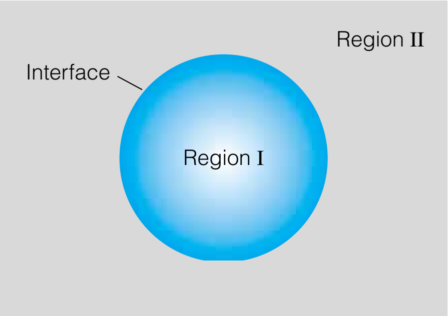


Figure 22.6 Region I is the liquid and region II is vacuum or some gas. The interface separates the two regions. The Laplace-Young equation predicts some of the properties of the liquid droplet.

22.13 is a fundamental equation for the behavior of an interface and is called the *Laplace-Young equation,* after Pierre-Simon Marquis de Laplace, a French mathematician, and Thomas Young, an English scientist whose work was also considered in Chapter 9.

How can we use equation 22.13? First, consider a droplet of liquid as shown in Figure 22.6. Regions I and II are marked for reference. Just by considering the figure and equation 22.13, there is an implication that the pressure in region I is greater than the pressure in region II. Consider why this is so. Surface tension is always positive, and the derivative $(\partial A/\partial V_{\text{I}})$ is also positive, always: as the volume of a region increases, so does its area. Therefore, the right side of equation 22.13 is always positive, so the difference $(p_{\text{I}} - p_{\text{II}})$ must always be positive. The only way for this to be so is for p_{I} to be greater than p_{II}: the pressure inside the liquid is greater than the pressure outside the liquid.

If the droplet of liquid is in fact spherical, we can use expressions for the surface area and the volume of a sphere from geometry:

$$A = 4\pi r^2 \qquad V = \tfrac{4}{3}\pi r^3$$

where r is the radius of the droplet. Because area and volume are dependent on another variable, the radius, we can take differentials of A and V in terms of r and substitute those expressions into the Laplace-Young equation. We find that

$$dA = 8\pi r \cdot dr$$

for the differential of area in terms of radius. For the change in volume,

$$dV = 4\pi r^2 \cdot dr$$

Plugging these expressions into the Laplace-Young equation, we find

$$(p_{\text{I}} - p_{\text{II}}) = \gamma\left(\frac{8\pi r \cdot dr}{4\pi r^2 \cdot dr}\right)$$

By defining Δp as the change in pressure across the interface, the above equation simplifies to

$$\Delta p = \frac{2\gamma}{r} \tag{22.14}$$

If the system under consideration were a bubble (that is, a film with an inner and an outer surface) instead of a droplet, then both surfaces would contribute a surface energy (that is, surface tension) and equation 22.14 would be

$$\Delta p = \frac{4\gamma}{r} \tag{22.15}$$

which is twice that for a droplet.

Equations 22.14 and 22.15 have some interesting applications. If there are unbalanced pressures in a system, then something usually happens. For example, in the case of a simple gas-in-a-piston system, unbalanced internal and external pressures cause irreversible expansions or contractions of the system's volume. In the case of liquid droplets, equation 22.14 implies that the smaller the droplet, the greater the vapor pressure on the gas-phase side of the liquid-gas interface. This suggests that smaller droplets evaporate faster. This fact has implications for such differing topics as perfume spraying and gasoline engine performance. (There are other equations we can use to understand the behavior of liquid droplets further. We won't consider them here, but see the exercises at the end of the chapter for another example.)

Example 22.4

What is the change in pressure across the surface of a droplet of water having a radius of 0.100 mm? What if the droplet had a radius of 0.001 mm (that is, 1 μm)? The surface tension of water is 72.75 erg/cm^2.

Solution

Mathematically, this example is simple from a numerical perspective, but we must watch our units. Using equation 22.14:

$$\Delta p = \frac{2\gamma}{r} = \frac{2\left(72.75\ \dfrac{\text{erg}}{\text{cm}^2}\right)}{0.100\ \text{mm}}$$

We need to revise the units so that they are consistent and work out to units of pressure. First, convert the mm unit in the denominator to centimeters:

$$\Delta p = \frac{2\left(72.75\ \dfrac{\text{erg}}{\text{cm}^2}\right)}{0.100\ \text{mm}} \cdot \frac{10\ \text{mm}}{1\ \text{cm}} = 1.455 \times 10^4\ \frac{\text{erg}}{\text{cm}^3}$$

Notice how the complex fraction involving the units simplifies into a simpler fraction. Additionally, we recognize that 1 dyne, a unit of force, equals 1 erg/cm. (An erg is a unit of energy.) We substitute:

$$\Delta p = 1.455 \times 10^4\ \frac{\text{dyn}}{\text{cm}^2}$$

Force per unit area (that is, dyn/cm^2) is defined as pressure, but what pressure unit is this? If you consider the units dyne and centimeter, you can show that 1 dyn/cm^2 is one-millionth of a bar, the standard SI unit of pressure. Converting:

$$\Delta p = 1.455 \times 10^4\ \frac{\text{dyn}}{\text{cm}^2} \cdot \frac{1 \times 10^{-6}\ \text{bar}}{1\ \dfrac{\text{dyn}}{\text{cm}^2}}$$

$$\Delta p = 0.01455\ \text{bar}$$

This might not seem like a large pressure difference, less than 2% of an atmosphere. But keep in mind that this is for a drop that's only 0.100 mm—a tenth of a millimeter—in radius! This is a substantial pressure difference for such a small droplet. Using 0.001 mm as a radius and repeating the substitution and conversions, we can show that

$$\Delta p = 1.455\ \text{bar}$$

This pressure difference is greater than atmospheric pressure!

The above example illustrates how large pressure differentials can be across an interface. Keeping in mind that pressure differentials will act to force liquid molecules to vaporize, one can see the advantage to vaporizing a liquid by separating it into as small a droplet as possible (a process misleadingly called *atomization*).

Interfaces also exist between liquid and solid phases. Under certain conditions their behavior is governed by surface tension effects. Consider a small droplet of a liquid on a surface. The way the droplet behaves depends on the

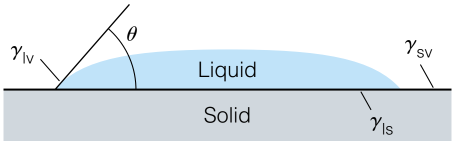
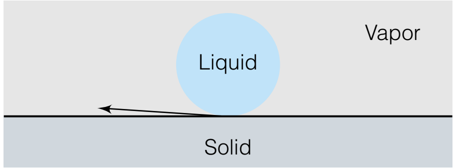
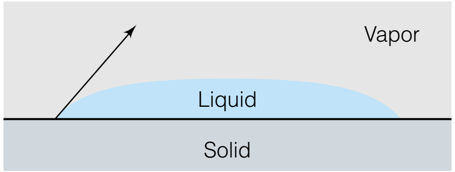


Figure 22.7 A liquid on a solid surface has a behavior dictated by three interfaces: the one between liquid and solid, the one between liquid and vapor, and the one between vapor and solid. The tangential angle that the liquid's edge makes with the surface is defined as the contact angle θ.



(a) γ_{lv} very high



(b) γ_{lv} very low

Figure 22.8 (a) If a liquid does not wet a solid surface at all, the liquid would (ideally, in the absence of gravity and other effects) be a small sphere on the solid surface. In this case, the contact angle approaches 180°. (b) If a liquid wets a solid surface very well, it would spread out over the solid and have a contact angle approaching 0°.

surface energies at several interfaces: the liquid-solid interface, the liquid-vapor interface, and the vapor-solid interface. At each interface, a different surface tension can be defined. Figure 22.7 shows an idealized drop on a surface and three different interfaces with three surface tensions. They are labeled $\gamma_{\ell s}$, $\gamma_{\ell v}$, and γ_{sv} for the liquid-solid, liquid-vapor, and solid-vapor interfaces, respectively. Note that although the liquid and vapor are the same chemical species, the solid may be a different chemical species.

Surface tension is a planar effect. It acts at a surface, which at any infinitesimal point can be marked with a tangent line. For flat liquid-solid and vapor-solid interfaces, these tangents are coplanar with the interface: the flat surface is where surface tension exists. For the liquid-vapor interface, because this surface is curved, the surface tension acts colinearly to a tangent to the curve. The tangent at the edge of the liquid-solid interface (that is, at the edge of the droplet) is drawn as a solid line in Figure 22.7, and the angle that this tangent makes with the solid surface is defined as θ. This angle θ is called the *contact angle.*

Why have we defined parameters this way? Consider what Figure 22.7 would look like if, for example, the surface tension of the liquid-vapor interface was very, very high compared to the other surface energies. The droplet would take on an almost spherical shape, as shown in Figure 22.8a. In this case, the contact angle is almost 180°. On the other hand, what if the surface tension of the liquid-vapor interface was comparable to the other surface energies? The droplet would then spread out substantially, as shown in Figure 22.8b. In this extreme, θ would be almost 0°. In this second instance, we say that the liquid is *wetting* the solid.

The point here is that the behavior of the liquid on the solid will be dependent on the relative magnitudes of the three interfacial surface tensions. In 1805 Thomas Young deduced an expression, later derived by A. Dupré in 1869, that relates the three surface tensions and the contact angle:

$$\gamma_{sv} = \gamma_{\ell s} + \gamma_{\ell v} \cos \theta \qquad \textbf{(22.16)}$$

This equation is called the *Young-Dupré equation.* It can actually be considered as a balance of three vectors: the solid-liquid interfacial tension pulling in one direction, and the liquid-solid and liquid-vapor tensions pulling in the other direction. But in the case of the liquid-vapor surface tension, only its component along the liquid-solid interface contributes to the balance of forces. The term cos θ accounts for that component.

The Young-Dupré equation is useful in predicting what is necessary to wet or to not wet a surface with a liquid. In terms of cos θ, equation 22.16 is rewritten as

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{\ell s}}{\gamma_{\ell v}} \qquad \textbf{(22.17)}$$

If you want a liquid to wet a surface (that is, $\theta \approx 0$, therefore $\cos \theta \approx 1$), a balance is required between the numerator and denominator of equation 22.17; that is, $\gamma_{sv} - \gamma_{\ell s}$ should be approximately equal to $\gamma_{\ell v}$. For example, solders are alloys whose liquids wet other metals because surface tensions have the appropriate values. By the same token, detergents and soaps help water wet solids (like synthetic fabrics) because they reduce the surface tension of water to the appropriate point.

Surface tension effects also show themselves in systems where a cylindrical solid surface is present. A very narrow cylindrical surface is called a *capillary.* What happens if a capillary is immersed into a liquid? The surface tension that

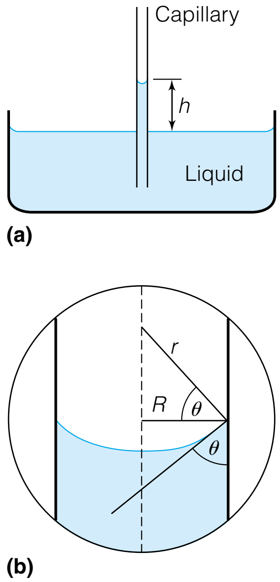


Figure 22.9 If a liquid wets a solid, then it will rise inside a small cylindrical tube of the solid material. (a) The net effect of capillary action. (b) The liquid inside the capillary forms a meniscus that makes a certain contact angle with the wall. See text for definitions of the variables.

exists at the liquid-vapor interface will act according to the Laplace-Young equation:

$$\Delta p = \frac{2\gamma}{r}$$

That is, there will be a pressure differential on either side of the liquid surface. Depending on the wettability of the surface, one of three things will happen. First, if surface tensions are balanced, nothing might happen; we will not consider this possibility further. Second, if the liquid wets the capillary surface, then the surface of the liquid in the capillary is curved as shown in Figure 22.9a, and the level of the liquid inside the capillary rises due to Δp, the pressure differential across the curved liquid surface. In fact, the liquid will rise until its height inside the capillary exerts a pressure equal to the Δp value from the Laplace-Young equation. This pressure is related to the force due to gravity of the column of liquid divided by the circular area of the capillary. This pressure is equal to the product of the liquid's density ρ, the gravitational constant g, and the height of the column in the capillary h:

$$\Delta p = \rho g h$$

It is therefore easy to determine how high this *capillary rise* will be:

$$\rho g h = \frac{2\gamma}{r}$$

or, rearranging for the height of the capillary rise:

$$h = \frac{2\gamma}{\rho g r} \tag{22.18}$$

The close-up in Figure 22.9b also shows that we can rewrite equation 22.18 in terms of the inner radius of the capillary, defined as R. If the surface of the liquid is spherical, then the radius of the curved meniscus and the radius of the capillary are related by

$$R = r\cos\theta$$

where θ is the contact angle. Substituting into equation 22.18:

$$h = \frac{2\gamma\cos\theta}{\rho g R} \tag{22.19}$$

If surface tensions are known from other measurements, equation 22.19 is an easy way to determine contact angles of liquids. It also shows that capillary rise will be larger if the capillary radius R is smaller.

The third possibility is that the liquid does not wet the surface. In that case, the meniscus of the liquid surface is inverted, as shown in Figure 22.10. Here, we see that the contact angle is greater than 90° and the cosine of that angle is negative. Therefore, the height of the column is negative and the liquid experiences a *capillary depression.* Mercury is a liquid that shows a capillary depression.

Capillary action, either rise or depression, is significant only for cylinders having small radii. If the capillary is wide enough to provide sufficient flat surface for the liquid, then capillary action is negligible.

Capillary action is found in many everyday settings. Paper towels, coffee filters, and tea bags work because of capillary action. Certain synthetic fabrics are uncomfortable in humid weather due to a lack of capillary action. Waterproofed

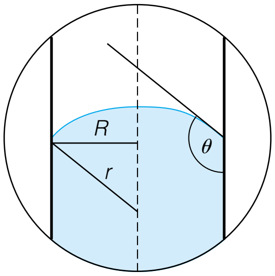


Figure 22.10 Capillary depression is seen when a liquid does not wet the solid material of a capillary. In this case, the diagram in Figure 22.9a would show the liquid in the capillary *below* the level of the liquid in the container. The meniscus in this case is inverted.

fabrics are made so by a coating or by using fabric fibers that do not show capillary action. All of these examples are ultimately based on surface effects.

22.4 Surface Films

Some systems can be defined as having a very thin film on the surface of a bulk material. For example, a tiny drop of oil will spread over a larger amount of water and produce some wonderful optical effects (caused by interference of light reflecting off the top and bottom interfaces of the thin oil film). A film that is one molecule thick is called a *Langmuir-Blodgett film.* (Irving Langmuir, an American physical chemist who worked for General Electric, pioneered the study of monomolecular films in 1918; his work was improved upon by another GE scientist, Katherine Blodgett, in 1934.) If suspended over water, these films are usually composed of materials that are water-insoluble and have a negligible vapor pressure.

In the case of a surface film composed of a specific amount of material, a sort of surface tension can be measured, using an experimental setup similar to that in Figure 22.2. In this case, however, the "surface tension" measures the ability of the molecules to compress or spread apart as the area of the film is changed. For surface films, a *surface pressure* π is defined as the difference between the surface tension $\gamma°$ of the pure solvent (usually water) and the surface tension γ of the solvent with the surface film on it:

$$\pi = \gamma° - \gamma \tag{22.20}$$

The surface pressure π varies tremendously with the area that a film is constrained to; see Figure 22.11 for a plot of π for various materials versus A, the area of coverage per molecule. In such a plot, a film of a certain amount of material is compressed or expanded, and the surface pressure is measured. In regions where each molecule is calculated to cover an area larger than itself, the surface pressure can be approximated by the equation

$$\pi A = RT \tag{22.21}$$

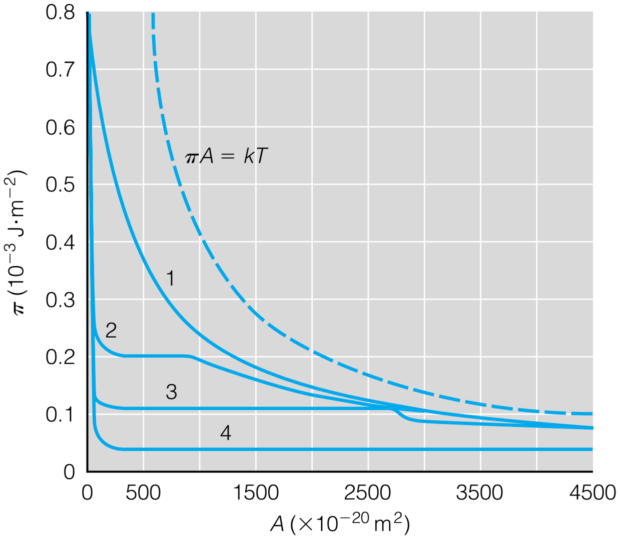


Figure 22.11 Surface pressure π versus area. For each material, the x-axis corresponds to the average area per molecule in the film. *Source:* Ya. Gerasimov, *Physical Chemistry,* Mir Publishers, Moscow, 1974.

Note the resemblance to the ideal gas law! Note also how the dotted line in Figure 22.11 mimics the hyperbolic curve of an inverse relationship between π and A, that is, Boyle's law. In these regions, each molecule can wiggle around independently of the others, and can be modeled as a sort of two-dimensional gas.

In regions where each molecule covers an area approximately equal to its own area, π is relatively constant. The size of these regions is highly dependent on the molecule making up the film. However, if the film is compressed beyond a certain point, the surface pressure increases dramatically, as shown on the left side of Figure 22.11. In these regions the surface film is forced into a multimolecular film, instead of a monomolecular film. The surface pressure thus represents the surface energy needed to force layers of molecules over each other.

Surface films are very common, although they may be easily overlooked. Oil on water has already been mentioned as a type of surface film. One very important surface film is a cell membrane. As seen in Figure 22.12, cell membranes are films of lipids that exist on the surfaces of protoplasm. The physical and chemical properties of these films are crucial to the ability of the cells to maintain a living state.

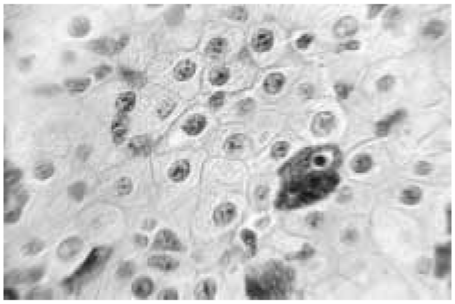


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Figure 22.12 In biological cells, the cell membrane is a film. The ability of the cell to function, or live, is highly dependent on the ability of the cell membrane to work properly.

22.5 Solid Surfaces

All solids terminate their structure at some point. This termination is the surface of the solid. Consider the surface of any object near you right now (this page, for example). At the level of human perception, there seems nothing strange or unusual about the surface of the solid object.

Partly, that's because solid surfaces are so familiar to us. We don't bother to question whether they have any interesting or unique characteristics. Actually, many solids *don't* have interesting or unique characteristics. Any random object has a rather messy surface at the atomic or molecular level. (See Figure 22.13 for a close-up of a surface.) They are multi- or polycrystalline or even amorphous, yielding a random surface that is so complicated, so random, that there is very little to be *able* to understand about its behavior.

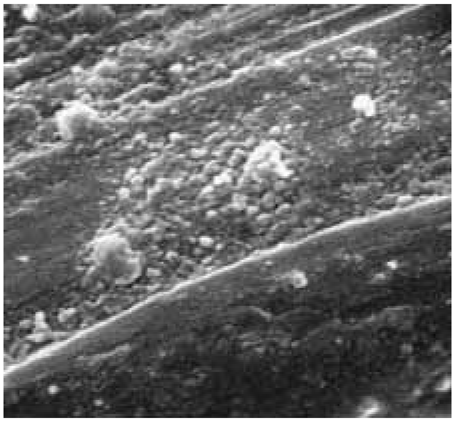

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Figure 22.13 Any random surface is actually very messy at the atomic level. This picture shows the surface of "smooth" stainless steele, magnified 10,000 times.

Therefore, in physical chemistry we require that the surfaces we study be a little more regular, a little more ordered. If we want to model a solid surface, that surface should be described by a relatively simple structure. It should not be a polycrystalline, random collection of solid particles. Model surfaces should be simple, regular, and easy to define.

We actually described planes of atoms in Chapter 21. We used *Miller indices* to define planes of atoms in a solid crystal. A proper model surface should be a simple plane of atoms, so we suggest that any good model surface should be described by the Miller indices of the plane to which the surface atoms belong.

Figure 22.14 shows our point. First, Figure 22.14a shows Miller index planes inside a solid crystal. The designation (110) is consistent with our under-

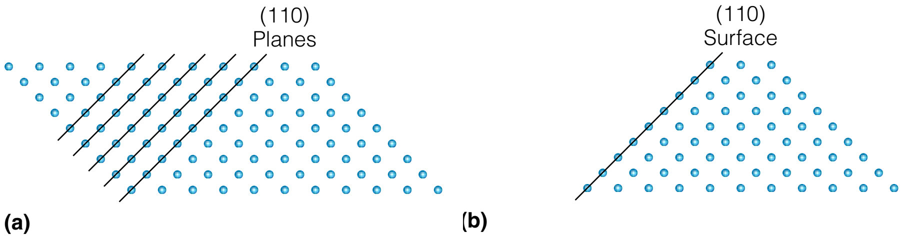
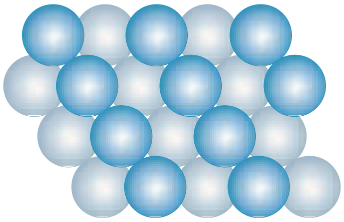
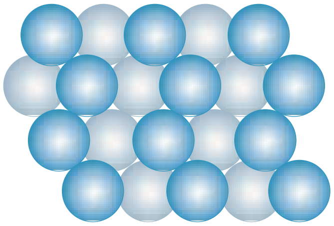


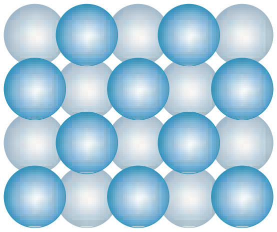
Figure 22.14 (a) Planes of atoms in a crystal are defined by Miller indices. (b) An exposed surface plane of atoms can also be described using the same Miller indices.



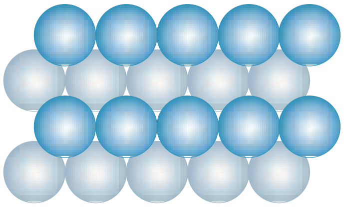
(a) fcc (111)



(b) hcp (0001)



(c) bcc (110)



(d) fcc (100)

Figure 22.15 Atomic arrangements for some crystals and the different Miller indices of the surface. In the diagrams, the darker atoms are the top layer, which has a different arrangement depending on the crystal lattice and ($hk\ell$).

standing of Miller indices, as defined and described in Chapter 21. Suppose we cut off one side of the crystal so that the atoms in the defined plane are now the surface of the solid. The Miller indices of that plane of atoms are sufficient to describe the surface of that solid. In this case, we can say that this surface is the (XYZ) plane of the crystal.

Miller indices are commonly used to describe surfaces of crystalline solids. Figure 22.15 shows some examples.

Example 22.5

Refer to Figure 22.16, which illustrates a surface of a body-centered cubic crystalline solid. What are the Miller indices of the surface indicated?

Solution

Since the crystal is a cubic solid, the unit cell parameters a, b, and c are equal. The surface plane indicated intercepts the a and b axes at one unit each, and does not intercept the c-axis at all. Another way of saying this is that the plane intercepts the c-axis at ∞. Miller indices are reciprocals of intercepts, so the Miller indices of this surface plane are $(\frac{1}{1}\,\frac{1}{1}\,\frac{1}{\infty})$ or (110). This surface is the (110) surface plane. Other surfaces of crystals can be labeled similarly.

As with liquid surfacces, the surface of a solid is associated with an energy. However, the term "surface tension" is not usually associated with solid surfaces. Instead, the term *surface energy* is used (although the concept is the same: it takes energy to increase the surface area of a solid). Table 22.2 lists some surface energies of solids. Generally, metals have relatively high surface energies, and ionic compounds have lower surface energies. Generally speaking, solids have higher surface energies than liquids, although a comparison of Tables 22.1 and 22.2 shows that at least one liquid (mercury) has a higher surface energy ("surface tension") than solids.

Surface energies for solids also vary depending on the arrangement of atoms making the surface plane; that is, surface planes having different Miller indices will have different surface energies.

The idea of different surface energies and an understanding of thermodynamics suggest that surfaces might tend to adopt the surface that has the lowest surface energy. Indeed they would *tend* to, but two factors work against this.

1. It is impossible for any solid except a cubic crystal to have the same Miller indices for all of its surfaces. This is because for any general solid,

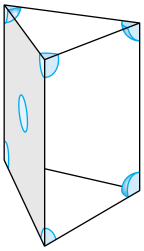


Figure 22.16 See Example 22.5. What are the Miller indices of the indicated surface of this body-centered cubic crystal?

Table 22.2 Surface energies of solids

Solid	Temperature (°C)	Surface energy (dyn/cm or erg/cm^2)[a]
gold	1027	1410
iron	1400	2150
LiF	−195	340
NaCl	25	227
KCl	25	110
MgO	25	1200
CaF_2	−195	450
BaF_2	−195	280

[a] To convert to units of J/m^2, multiply by 1×10^{-3}.

the three crystalline axes are spatially different. Even for a cubic crystal, the exception applies only to the planes that contain the three crystalline axes of cubic crystals. (However, for planes that are not coincident with the axes, this exception does not apply.)

2. Solids are, well, solid. Their very definition is that their atoms or molecules are in fixed positions. Therefore, even if a surface is not the lowest-energy surface, the surface usually remains in that higher-energy structure. (In some situations, surface rearrangements occur that lower the surface energy, but we will not consider these in detail here. See Figure 22.17 below and the discussion of it in the text, however.)

Created by Dr. George B. Hares, Research Fellow and Mr. Henry E. Hagy, Senior Research Associate (ret.), Corning, Inc.

Figure 22.17 Annealing a solid allows the atoms or molecules to adopt a different, more stable structure. The first picture shows the solid (glass) before annealing, and the second picture shows the same solid after annealing.

In some cases, the second factor can be overcome by heating the solid, a process called *annealing*. Annealing implies that a solid is heated to a temperature *below* its melting point so the formation of a liquid phase is avoided. However, enough thermal energy is usually present that some of the solid atoms or molecules can slowly move, or *diffuse*, a short distance and adopt a lower-energy structure. The solid is heated and then cooled slowly, giving the atoms or molecules time to adopt a new structure. Annealing is common in the production of glass objects, so that the glass molecules can form a stable, less-strained solid structure. Figure 22.17 shows an example of how annealing leads to lower-energy solid structures; similar effects are seen in solid surfaces as well.

So far in our discussion of solid surfaces, we have assumed that the surface of a solid is actually formed by the solid material itself. For example, a piece of solid iron metal has a solid surface that is composed of iron atoms, with bulk iron on one side of the surface and air or atmosphere on the other side, right? Unfortunately, in this instance and for almost all other surfaces, this is definitely not the case. In reality, at the atomic and molecular level, solid surfaces are very messy.

Why is that? Well, look at Tables 22.1 and 22.2 and compare the surface energies/tensions of solids and liquids. Note that many liquids—including water—have much lower surface energies than solids. Applying the idea that materials tend toward lower energies, in a system of solid and liquid the surface will be covered with the lower-surface-energy liquid. Consider what this means at the atomic and molecular level for a solid surface: when exposed to an environment, the "surface" of the solid is actually covered with materials that tend to lower the total surface energy. Consider a piece of crystalline magnesium oxide exposed to a moist environment. MgO has a surface energy of about 1200 erg/cm^2 and water has a surface energy of about 73 erg/cm^2, so the low-energy scenario has a thin layer of water on the surface of the crystalline MgO. This water can be as thin as a single monolayer (that is, a surface film) and is considered *adsorbed* on the solid. (The word *adsorbed* should be compared to be word *absorbed*, which would mean that one material has been incorporated inside something else, like water in a sponge.) Consider all of the surfaces around you: at the atomic and molecular level, they all have something adsorbed on them. Thus, what you may be perceiving as the surface of a plastic laminate tabletop isn't actually plastic, but a surface that has water or other organic, silicone, fluorocarbon, or other low-energy material as the true "surface" material.

Example 22.6

Consider Tables 22.1 and 22.2. A crystal of sodium chloride, NaCl, is exposed to an air sample that has water vapors, ethanol vapors, and diethyl ether vapors. (Water, ethanol, and diethyl ether are all liquids at room temperature.) Ignoring the possibility of minimum-energy interactions between the three vapors (that is, azeotropes and the like), what would you predict to be the true surface structure of NaCl? (Ignore interactions between the NaCl and the vapors.)

Solution

If we apply the ideas immediately above, the preferred surface structure would have the minimum surface energy. Comparing the surface tensions of the liquid phases associated with the vapors, we find that diethyl ether has the lowest surface tension. Thus, we suggest that the surface of NaCl might actually be covered with diethyl ether molecules. (Apart from its instructiveness, this example is extremely naive. In reality, ion-dipole interactions would contribute considerably to the formation of a molecular film on the surface of the solid. In extreme cases—like NaOH—energies of solvation are so negative that enough water is adsorbed to form a solution; such compounds are described as *deliquescent.*)

The above example illustrates a point: real surfaces, exposed to real environments, are very messy at the molecular level. Just about any surface you can see is covered with molecules that are not of the material itself.

It actually takes special effort to get surfaces that are *clean*; that is, free from adsorbed contaminants. Among other things, it is necessary to expose a surface to a very, very high vacuum. *Ultrahigh vacuums,* which are usually considered to involve pressures less than 1×10^{-8} torr, are necessary to minimize the number of gas molecules that come in contact with a surface and form a low-surface-energy layer. This might not sound like an "ultrahigh" vacuum, even though it represents about one hundred billionth of an atmosphere. From considerations related to the kinetic theory of gas, we can show that even at about one millionth of a torr, in about 1 second enough gas molecules strike a surface to form a single molecular monolayer. A pressure of 1×10^{-8} torr suggests that the monolayer formation takes about 100 seconds, or less than 2 minutes: not a clean surface for very long! Pressures of 1×10^{-11} to 1×10^{-12} torr are sometimes necessary, and they require special vacuum technology to achieve.

The term *exposure* is defined as the product of the pressure of gas in contact with a surface and the time the surface is exposed to that pressure:

$$\text{exposure} \equiv (\text{pressure}) \times (\text{time}) \tag{22.22}$$

The unit of exposure is the *langmuir.* A pressure of 1×10^{-6} torr applied for 1 second gives a surface an exposure to molecules that is defined as 1 langmuir (1 L, not to be confused with 1 liter):

$$1 \text{ langmuir} \equiv 1 \times 10^{-6} \text{ torr} \cdot \text{s} \tag{22.23}$$

For scientists trying to study clean surfaces, this is a useful unit for communicating exposure pressure and time, both of which relate to how long a surface can really be considered "clean." Roughly speaking, a monolayer of adsorbed atoms or molecules forms when a surface experiences an exposure of 1 langmuir.

Example 22.7

A clean surface is exposed to a pressure of 2.0×10^{-11} torr. How long will it take for about one-half of a monolayer to form on the surface?

Solution

One-half of a monolayer requires an exposure of approximately 0.5 L. Using equation 22.22 and the definition from equation 22.23:

$$0.5\ \text{L} = (2.0 \times 10^{-11}\ \text{torr}) \times (\text{time}) \times \frac{1\ \text{L}}{1 \times 10^{-6}\ \text{torr·s}}$$

The last term is a conversion factor between the units involved and comes straight from equation 22.23. We solve this equation algebraically for time:

$$\text{time} = \frac{0.5\ \text{L}}{(2.0 \times 10^{-11}\ \text{torr}) \times \dfrac{1\ \text{L}}{1 \times 10^{-6}\ \text{torr·s}}}$$

The langmuir and torr units cancel; the only remaining unit, seconds, is in the denominator of the denominator, which makes it in the numerator. Solving numerically:

$$\text{time} = 2.5 \times 10^{4}\ \text{s}$$

It will take almost 7 hours for one-half of a monolayer to form. This example shows that at such low pressures, surfaces can be kept relatively clean for quite a while if an ultrahigh vacuum is maintained.

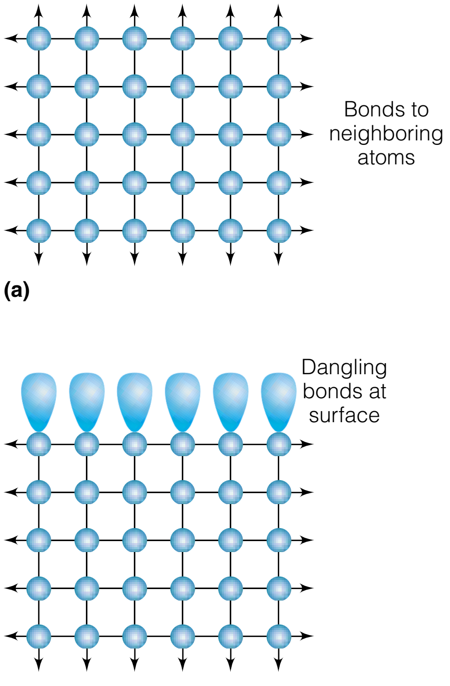


Figure 22.18 (a) In the bulk of a solid, atoms interact with other atoms all around them. The arrows imply that bonding continues in that direction to other atoms. (b) At the surface, atoms interact with other atoms in all directions except one. In that direction, there is an "unsatisfied" bond called a dangling bond that can easily interact with other chemical species. Compare this diagram with Figure 22.1, which shows the imbalance of forces that ultimately cause surface tension.

These calculations are approximate because they assume that any gas atom or molecule that hits a surface will stick there. In reality, this depends on the identity of the gas species, the identity of the surface, and the temperature of the gas and/or the surface.

The student should be aware that it takes special vacuum equipment to maintain an ultrahigh vacuum. First, a clean surface must be inside a special vacuum chamber that has no leaks—which is easier said than done. In addition, special vacuum pumps must be used to get to such high vacuums and stay there. The normal oil-filled rotary vacuum pump can only maintain a vacuum of about 10^{-4} torr or so, a full four orders of magnitude higher than what is necessary for ultrahigh vacuum. Special vacuum pumps (like turbomolecular pumps, titanium sublimation pumps, or liquid-helium-based cryopumps) are needed and can be extremely expensive.

Assume that we do, in fact, have a clean surface. What makes the surface so special that it has properties different from the bulk? The answer lies in understanding the chemical nature of a bulk solid. Figure 22.18a shows a two-dimensional solid in which the atoms are all connected to each other in all directions. That is, they are all bonding to their neighboring atoms. Figure 22.18b shows what happens when this two-dimensional solid is cracked so that a new surface is exposed to the environment. The atoms at the surface make bonds to the atoms in the bulk, but there are no atoms to bond with on the other side of the surface. The atoms at the surface have atomic orbitals that are not (as yet) interacting with—bonding to—any other atomic or molecular species. These empty orbitals, sometimes referred to as "dangling bonds," are very reactive and will interact extremely easily with other chemical species. This model accounts for several properties of surfaces, not just their ability to easily adsorb molecular species from the surrounding environment. Empty orbitals of adjacent atoms sometimes interact with each other, causing a slight rearrangement of the surface layer(s) so that the surface structure is somewhat different from the bulk. (This was alluded to earlier in the chapter.) Figure 22.19 shows an example of the structural rearrangement of a surface.

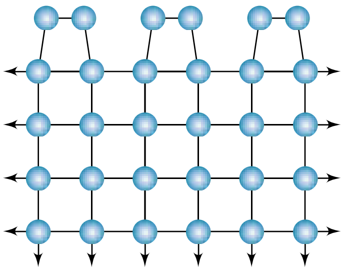


Figure 22.19 Sometimes the dangling surface bonds interact with each other. When they do, the exact structure of the surface can differ substantially from the bulk structure, as shown. This figure is merely illustrative; what happens in real surfaces depends on the material.

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Figure 22.20 The Swedish chemist Jöns Jakob Berzelius (1779–1848) was considered a world authority on chemistry in his time. In 1813, he suggested the use of alphabetical symbols to stand for elements in chemical formulas, thereby getting away from alchemical symbols. He also invented the term "catalysis" to describe the speeding up of chemical reactions by the presence of nonreactive components.

22.6 Coverage and Catalysis

In the 1830s, the Swedish chemist Jöns Jakob Berzelius (Figure 22.20) coined the term "catalysis" to describe the effect of a substance that increases the speed of a chemical reaction but is not itself consumed by the reaction. The substance itself is called a *catalyst.* (By contrast, an *inhibitor* is a substance that decreases the speed of a reaction.) In modern terms, a catalyst provides a different pathway for a chemical reaction to take place, one that has a lower activation energy, thereby increasing the rate of reaction. Ideally, a catalyst does not appear in the overall stoichiometry of the reaction and is not used up during the course of the reaction. In reality, most catalysts eventually lose their effectiveness due to various mechanisms including poisoning.

Catalysis can be separated into two types, *homogeneous catalysis* and *heterogeneous catalysis.* The difference depends on the phases of the chemical reaction and the catalyst. If all substances including the catalyst are in the same phase, it is considered homogeneous catalysis. Examples include aqueous-solution reactions that are catalyzed by acid (H^+ ions) or base (OH^- ions), and gas-phase reactions like the breakdown of ozone, O_3, by chlorine atoms in the upper atmosphere.

If catalysis occurs at a phase boundary because reactants and catalyst are in different phases, it is heterogeneous catalysis. Examples include the decomposition of NO_x pollutants by catalytic converters in cars and the formation of H_2O from H_2 and O_2 gases in the presence of finely divided metal powders.

In both of the examples given for heterogeneous catalysis, gaseous reactants are interacting with a solid catalyst and making products. The interaction must be occurring at the surface of the solid. In order to understand how a surface catalyzes a reaction even in a simplistic sense, we need to understand how to model interactions between gases and surfaces.

It is a good assumption to think that the rate of the catalyzed reaction is related to the rate at which the gas reactant(s) interact with that surface. That is, the rate of the catalyzed reaction must be related to the rate at which reactant molecules are adsorbed on the surface:

$$\text{gas reactant} \xrightarrow{\text{catalyst}} \text{gas reactant (adsorbed)} \qquad \text{Rate}_{\text{ads}}$$

Let us consider processes that involve the adsorption of a single gaseous species on a solid surface. We will make two simplifying assumptions. First, we assume that the gas molecules that are adsorbed directly onto the surface are the ones that react faster, that is, are catalyzed. From this, we conclude immediately that the maximum amount of gas that can be adsorbed and catalyzed would be a complete monolayer of gas molecules. The variable *coverage* is defined as the decimal fraction of possible positions on the surface that have an adsorbed gas molecule on them. Coverage is symbolized by the Greek letter θ and varies between 0 (for no coverage) to 1 (for a complete monolayer of coverage). Molecules that might be adsorbed on top of a monolayer are assumed to not experience any catalysis effects of the surface.

Second, we assume that the adsorption of gas molecules is an elementary process so that the rate of adsorption, Rate_{ads}, can be determined directly from the stoichiometry of the reaction. The rate of adsorption is therefore directly proportional to the concentration of the gas reactant, which we will designate [gas]. But the rate of adsorption is also proportional to the amount of surface positions available to adsorb onto. These surface positions are called *sites of adsorption.* If the coverage is θ, then the number of sites available (that is, not covered) is given by $(1 - \theta)$. We can therefore write the rate of adsorption as

$$\text{Rate}_{\text{ads}} = k_{\text{ads}} \cdot [\text{gas}] \cdot (1 - \theta) \tag{22.24}$$

After reaction on the surface, the gas molecules have to leave the surface, or *desorb*. The rate of desorption is assumed to be a zeroth-order reaction that is related only to the coverage θ:

$$\text{Rate}_{\text{des}} = k_{\text{des}} \cdot \theta$$

where the subscript "des" relates the variables to the desorption process. If the adsorption and desorption rates are equal, the reaction is occurring at some steady pace and the adsorption and desorption rates are equal to each other:

$$\text{Rate}_{\text{ads}} = \text{Rate}_{\text{des}}$$

$$k_{\text{ads}} \cdot [\text{gas}] \cdot (1 - \theta) = k_{\text{des}} \cdot \theta \tag{22.25}$$

We can use the above equation to algebraically solve for the coverage θ:

$$\theta = \frac{k_{\text{ads}} \cdot [\text{gas}]}{k_{\text{ads}} \cdot [\text{gas}] + k_{\text{des}}} \tag{22.26}$$

The equilibrium constant for the adsorption/desorption process is given by

$$K = \frac{k_{\text{ads}}}{k_{\text{des}}}$$

and equation 22.26 can be rewritten in terms of K to get

$$\theta = \frac{K \cdot [\text{gas}]}{K \cdot [\text{gas}] + 1} \tag{22.27}$$

Equation 22.27 shows that θ will always be less than 1 because the numerator will always be less than the denominator.

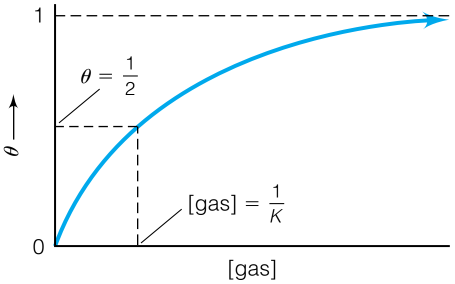


Figure 22.21 If adsorption of a gas (or a dissolved solute) on a surface follows the Langmuir isotherm, a plot of coverage θ versus [gas] should have this shape of curve. At θ of 0.50, [gas] should equal $1/K$, in accordance with equation 22.27.

Equations 22.26 and 22.27 define what are called *Langmuir isotherms.* (The word "isotherm" is used to emphasize a constant-temperature condition in these types of studies.) Although θ is difficult to measure directly, it can be done indirectly by measuring adsorbed mass (so that the maximum mass adsorbed is equivalent to a θ of 1) or by titration methods (so that the amount of an acid adsorbed can be measured and related to θ). A plot of θ (or a related variable) versus [gas] can be made, like the one in Figure 22.21. The equilibrium constant K can be estimated from the graph; equation 22.27 shows that for θ to equal $\frac{1}{2}$, $[\text{gas}] = 1/K$.

Equation 22.27 can also be rewritten in terms of the reciprocal of the coverage θ to get

$$\frac{1}{\theta} = \frac{K \cdot [\text{gas}] + 1}{K \cdot [\text{gas}]} \quad \text{or} \quad \frac{1}{\theta} = \frac{1}{K \cdot [\text{gas}]} + 1 \tag{22.28}$$

The second equation in Equations 22.28 has the general expression for a straight line, where y equals $1/\theta$, x is $1/[\text{gas}]$, and the slope is $1/K$. Thus, $1/\theta$ (or variables proportional to it, like reciprocals of mass adsorbed or acid not titrated) plotted versus $1/[\text{gas}]$ should give a straight line, as shown in Figure 22.22. In terms of actual measurements, if we define a change in mass of a surface sample, Δm, as proportional to the coverage θ:

$$\Delta m \propto \theta$$

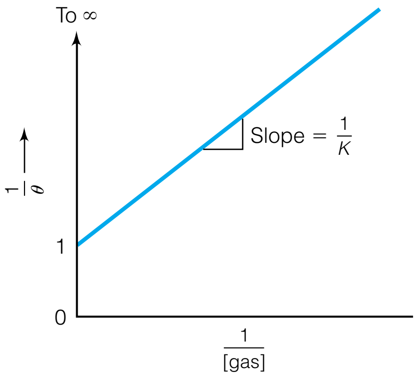


Figure 22.22 Another way to plot the adsorption of a gas (or dissolved solute) on a surface if it follows a Langmuir isotherm. In this case, the straight line should have a y intercept of 1 and a slope of $1/K$. See equation 22.28.

and then define a proportionality constant κ (the Greek letter kappa) to relate the two:

$$\Delta m = \kappa \cdot \theta \quad \text{or} \quad \frac{1}{\Delta m} = \frac{1}{\kappa} \cdot \frac{1}{\theta}$$

then we can rewrite equation 22.28 in terms of a measurable parameter:

$$\frac{1}{\Delta m} = \frac{1}{\kappa \cdot K \cdot [\text{gas}]} + \frac{1}{\kappa} \tag{22.29}$$

Equation 22.29 shows that if we plot the reciprocal of the change in mass, $1/\Delta m$, as a gas is adsorbed on a surface versus the reciprocal of the concentration of the gas, we will get a straight line whose y intercept is the reciprocal of the proportionality constant κ. Using this value, we can use the slope of the plot [which equals $1/(\kappa \cdot K)$] to determine the equilibrium constant of the adsorption/desorption process. Also, instead of Δm, we can use a change in concentration; the concepts behind equation 22.29 remain the same.

Finally, since the y intercept corresponds to an infinite value of [gas] (so that 1/[gas] equals 0), its value should correspond to a coverage of 1. Knowing the approximate size of the molecule, we can determine how many molecules are adsorbed as well as the approximate surface area of the solid. The proportionality constant κ thus acts as the conversion factor between mass adsorbed and surface area of the solid. The following example shows how to use some of these ideas.

Example 22.8

One application of adsorption on surfaces is to measure the ability of activated charcoal to adsorb acid. (Activated charcoal, a form of treated carbon, is very porous and is used to adsorb impurities from water. Its use in aquariums typifies this behavior.) In a lab experiment, a student mixes a given amount of powdered charcoal into a series of acetic acid solutions. The acetic acid solutions have different initial concentrations. Some of the acid is adsorbed onto the charcoal. By taking aliquots after equilibrium is established, the student determines the change in acid concentration. Plot a Langmuir isotherm for the experimental data and determine the equilibrium constant for the adsorption. The experimental data are as follows:

Original concentration (M)	Change in concentration (M)
0.7001	0.00665
0.3694	0.00588
0.1515	0.00553
0.0437	0.00283
0.0169	0.00153

Solution

In order to use equation 22.29 to plot an isotherm and determine a proportionality constant κ, we need to plot $1/\Delta c$, the inverse of the concentration change, versus 1/[acid]. The following table is determined from the experimental data given above:

1/[acid]	$1/\Delta c$
1.428	150.
2.708	170.
6.601	181
22.9	353
59.2	654

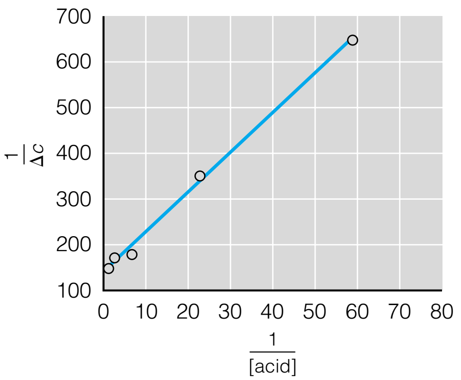


Figure 22.23 Plot of data for Example 22.8. The y intercept equals $1/\kappa$, the inverse of the proportionality constant, whereas the slope equals $1/\kappa \cdot K$. See Example 22.8 for details.

Figure 22.23 shows a plot of this data, with $1/\Delta c$ on the y-axis and $1/[\text{acid}]$ on the x-axis. A best-fit straight line is drawn, showing that the y intercept is approximately 141. According to equation 22.29, this is the value of $1/\kappa$. Taking the reciprocal, we find that κ is $\frac{1}{141}$, or 0.00709. Our best-fit straight line also has a slope of 8.45, which equals $1/(\kappa \cdot K_{eq})$. Having solved for κ, we use algebra to find a value for K, and get $K \approx 16.7$. If we had additional data—say, the size of the acetic acid molecule or the surface area of the charcoal—we could calculate the surface area or the molecule size, respectively.

The Langmuir isotherm is a common way of modeling gas- or liquid-phase molecules adsorbing on surfaces, but it isn't the only way. Another way to model the coverage versus the concentration of the adsorbing species is the *Freundlich isotherm,* which follows the equation

$$\theta = K \cdot [\text{adsorbing species}]^c \tag{22.30}$$

where K and c are experimentally determined constants. This equation is usually plotted in terms of its logarithm, which makes it

$$\log \theta = \log K + c \cdot \log\,[\text{adsorbing species}]$$

and has the form of a straight line. There are other isotherms defined for different heterogeneous systems. (Consult a text on surface science for more details.)

What if a reaction involves the adsorption of two different gas-phase species, A and B, onto a solid surface? In order to model those processes, we will have to define two different coverage variables θ_A and θ_B. If we assume that the adsorption and desorption of each process are in equilibrium, then we can rewrite equation 22.25, the equality of the adsorption and desorption rates, for each gas-phase species:

$$\begin{aligned} k_{ads,A} \cdot [A] \cdot (1 - \theta_A - \theta_B) &= k_{des,A} \cdot \theta_A \\ k_{ads,B} \cdot [B] \cdot (1 - \theta_A - \theta_B) &= k_{des,B} \cdot \theta_B \end{aligned} \tag{22.31}$$

By defining two equilibrium constants K_A and K_B in terms of the adsorption and desorption rate constants like we did earlier, we can solve for the two coverages. We give their expressions without showing the algebra:

$$\begin{aligned} \theta_A &= \frac{K_A \cdot [A]}{K_A \cdot [A] + K_B \cdot [B] + 1} \\ \theta_B &= \frac{K_B \cdot [B]}{K_A \cdot [A] + K_B \cdot [B] + 1} \end{aligned} \tag{22.32}$$

These expressions define *Langmuir-Hinshelwood isotherms.* (Cyril Norman Hinshelwood was a British chemist who won a 1956 Nobel Prize for studying chemical reaction mechanisms.)

Finally, suppose a diatomic gas is adsorbed on a surface and the first step is for the molecule to dissociate and occupy two sites, one by each atom:

$$A_2\,(g) \overset{\text{surface}}{\rightleftharpoons} 2A \overset{\text{surface}}{\rightleftharpoons} 2A\,(\text{adsorbed})$$

If these processes are in equilibrium, then the stoichiometry of the reaction would affect the expression for the coverage θ by the A atoms. Instead of equation 22.27, one would get for a Langmuir isotherm

$$\theta = \frac{K^{1/2} \cdot [A_2]^{1/2}}{K^{1/2} \cdot [A_2]^{1/2} + 1} \tag{22.33}$$

Table 22.3 Heat of adsorption for gases on surfaces

Gas	Solid surface	$\Delta_{ads}H$ (kJ/mol)
O_2	Cu(110)	205
O_2	Pd(110)	200–350
O_2	Pt(100)	187–290
H_2	Ni(111)	95
H_2	Pd(111)	87
H_2	Pt(100)	~40
H_2	Pt(111)	75
H_2	W(211)	192
CO	Cu(100)	64–48
CO	Ni(110)	16–191
CO	Ni(111)	98–111
CO	Pd(100)	151
CO	Pd(111)	125
CO	Pt(100)	134
CO	Pt(110)	105–133

Source: G. A. Somorjai, *Chemistry in Two Dimensions: Surfaces,* Cornell University Press, Ithaca, N.Y., 1981.

Now that we have a way to model the adsorption of gas species on a surface, we should consider how adsorbed species interact with a surface. There are two descriptions of molecule-surface interaction, differing mainly in terms of degree of interaction. In *physisorption,* molecules interact with surfaces in a weak and general way. It could be as simple as a van der Waals or dispersion interaction that keeps a molecule on a surface, like molecules of methane (CH_4) or diatomic nitrogen (N_2) on metal surfaces, or organic residues all over the place. Or, it could be a dipole interaction with a surface atom, which is how water molecules adsorb so easily on most surfaces.

In *chemisorption,* the strength of interaction between molecules and a surface is high enough to be considered a bona fide chemical (covalent) bond. It is not unusual for the strength of chemisorption to rival a true chemical bond. Diatomic oxygen, for example, adsorbs on many metals with a chemisorption strength of over 500 kJ/mol!

Chemisorption and physisorption are usually studied by measuring (directly or indirectly) the coverage of a surface versus the temperature. The lower the temperature needed to reduce the coverage of a surface, the lower the energy of interaction between gas molecule and surface. Energies of interactions are usually listed as heats of adsorption, or $\Delta_{ads}H$. They are typically listed as positive numbers, although in all cases the process itself is *exothermic.* Table 22.3 lists some $\Delta_{ads}H$ values for different gases and surfaces; keep in mind that these are inexact numbers. Differentiation between physisorption and chemisorption is inexact and is usually judged on the basis of the strength of interaction as well as structural considerations. For example, the energy of interaction between carbon monoxide, CO, and palladium is large enough to consider it as chemisorbed, but in many cases the distribution of CO on a surface is seemingly random with respect to the surface features, suggesting that it is physisorbed.

Chemisorption does differ from physisorption in a significant way. It is not unusual for chemisorbed molecules to break their chemical bonds and have the resulting fragments bond directly to surface atoms. By making chemical bonds to surface atoms, the fragments can satisfy their valence electron requirements. Figure 22.24 shows the difference between physisorption and chemisorption of a dihydrogen molecule. In Figure 22.24a, the hydrogen molecule is loosely bound to a surface point (and can have various orientations, depending on the surface identity, the temperature, and the coverage). However, in Figure 22.24b, the hydrogen atom's bond has broken and the individual H atoms are bonding directly to different surface atoms. The physisorption model could apply to H_2 adsorbing on the Ta(110) surface, where the energy of adsorption is about 40 kJ/mol, whereas the chemisorption model could describe H_2 on a W(111) surface, in which the energy of adsorption is two to three times higher.

The ability for surfaces to promote bond dissociation is a crucial part of understanding why surfaces can catalyze reactions. Many gas-phase reactions have some activation energy that must be overcome before reactants can form products. However, when interacting with a surface, activation barriers can be lowered significantly, speeding up the rate of (that is, catalyzing) the reaction.

The steps occurring at a surface, and their respective changes in energies ΔE, can be simplified and generalized as follows:

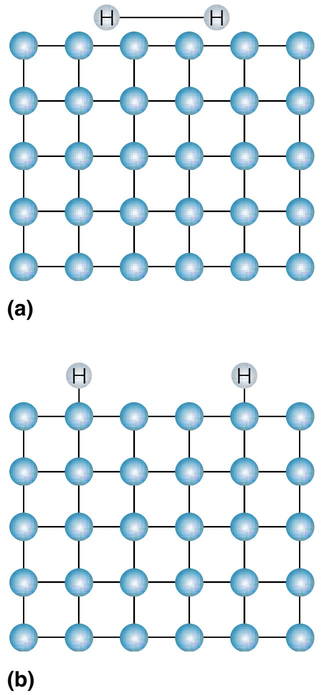


Figure 22.24 There is a fundamental difference between physisorption and chemisorption, shown here diagrammatically. (a) In physisorption, a molecule of hydrogen remains intact but is attracted to a surface due to van der Waals forces, London forces, or the like. (b) In chemisorption, chemical species are virtually bonded chemically to the surface. In the case of hydrogen, it is necessary to break the H–H bond for it to be chemisorbed. This is not always required: for carbon monoxide, the CO molecule might be as strongly bonded to the surface but still retain the C–O bond.

$$\text{gas molecule} \xrightarrow{\text{surface}} \text{physisorbed molecule} \qquad \Delta E = \Delta_{\text{ads}}H \text{ (exothermic)}$$

$$\text{physisorbed molecule} \xrightarrow{\text{surface}} \text{dissociated atoms} \qquad \Delta E = \text{bond energies (endothermic)}$$

$$\text{dissociated atoms} \xrightarrow{\text{surface}} \text{chemisorbed atoms} \qquad \Delta E = \text{bond energies (exothermic)}$$

In the second step, bond energies are broken, which is always endothermic. Conversely, in the third step bonds are formed, which is always accompanied by a release of energy (that is, exothermic). At this point, chemisorbed atoms can react on the surface with little or no activation energy:

$$\text{chemisorbed atoms} \xrightarrow{\text{surface}} \text{products} \qquad \Delta E = \text{bond energies (exothermic)}$$

Desorption of products is the final step of the catalyzed reaction.

In order to get to the last, no-activation-energy step, it is important that in the first three steps, the exothermicity be greater than the endothermicity. Otherwise the process is overall endothermic and, if one ignores entropy effects, not spontaneous. (There are some cases where entropy factors are important, but we will not discuss them here.) However, in some cases the energy balance is such that reactant molecules will spontaneously adsorb and dissociate, allowing them to react with little or no activation energy on the surface. Two examples are the reactions between H_2 and O_2 to make H_2O and H_2 and N_2 to make NH_3. In both cases, the presence of the right catalyst surface provides the right energy balance between endothermic and exothermic processes, and the reactions proceed relatively quickly. Without a catalyst, the rate of the reaction is barely perceptible.

Because of the interplay of the energetics of the first three reaction steps above, what acts as a good catalyst for one reaction may be a very poor catalyst for another! The H_2/O_2 reaction works well with a palladium or platinum catalyst, whereas the ammonia reaction uses an iron-based catalyst. Identification of the right catalyst for the right reaction is still an intense area of research.

Finally, catalysis is not confined to well-defined, Miller-indexed metal surfaces. One area of recent interest is in the use of clay minerals to catalyze reactions. You may think of "clay" as a rather gooey and unstructured material, but in reality it has a highly defined, three-dimensional structure. In some clays called *zeolites,* there are pores in which molecules can enter, and then be adsorbed. Figure 22.25 shows a diagram of what a pore within a zeolite clay looks like. Thanks in part to the three-dimensional structure of the pore, only the right reactant molecules can be adsorbed and a particular reaction promoted. In fact, it is thought that clay minerals such as these are the future of *designed* catalysts that can be used to promote any given chemical reaction—if the pore is just right.

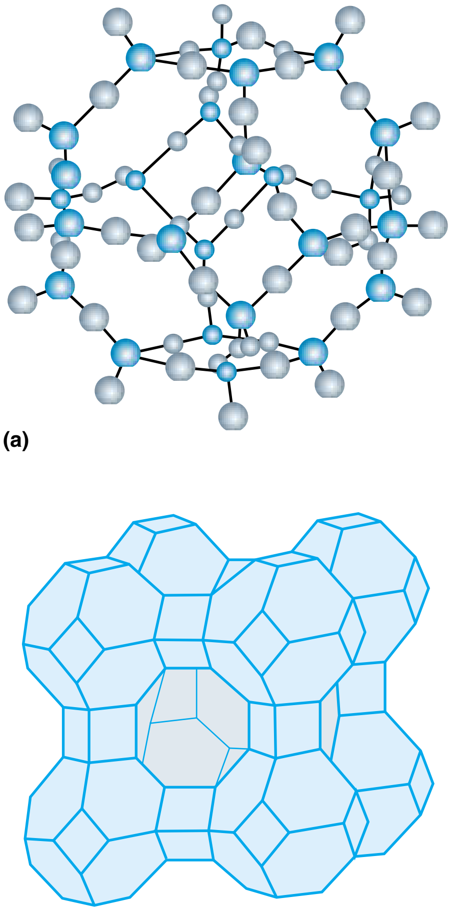


Figure 22.25 Certain clay minerals have catalytic properties. Clays are composed of aluminum oxide units interspersed with silicon oxide units, and can have pores for molecules to enter and react. (a) A common building block of aluminosilicate clays (the open spheres are O, the dark spheres are Si or Al). (b) Part of a zeolite structure, which is a common type of clay used in heterogeneous catalysis.

22.7 Summary

Surfaces are everywhere, and are more important in physical chemistry than they seem at first glance. A surface has different thermodynamic properties than a bulk material does. This is due to an imbalance in forces that are found at a surface. This imbalance is the root cause of things like surface tension and capillary action. Surfaces can be as thin as a single molecule, called a film. The behavior of that film is intimately related to the properties of surfaces in general.

For well-defined solids like crystals, the surfaces themselves can be well defined using Miller indices. (Solids are not always so well defined, but it is certainly easier to understand them when they are.) What we understand about them includes the fact that they can influence chemical reactions but not actually participate in the overall chemistry: they act as catalysts. The ability of a surface to act as a catalyst depends on several factors, including how easily a reactant molecule adsorbs onto the surface, how easily a molecule on the surface dissociates, and how easily the resulting atoms combine to make products. The right combination of reaction and surface can have a major influence on the rate of the reaction.

EXERCISES FOR CHAPTER 22

22.2 Surface Tension

22.1. Using the explanation of unbalanced forces as the source of surface tension, justify why it *requires* energy to increase the surface area of a liquid. Is there any circumstance in which energy is given off when increasing a liquid's surface area?

22.2. The surface tension of liquid mercury from Table 22.1 is 435.5 N/m. What is the value of γ(Hg) in units of dyn/cm?

22.3. The surface tension of chloroform, $CHCl_3$, is 27.1 dyn/cm. **(a)** How many joules does it take to increase the surface area of a pool of chloroform by 50.0 cm^2? **(b)** How many joules does it take to make a film of chloroform that has an area of 0.010 m^2?

22.4. Equation 22.6 defines surface tension in terms of Gibbs free energy. Borrowing an analogy from chemical potential, we submit that surface tension can also be defined in terms of enthalpy, internal energy, or Helmholtz energy. Write partial derivatives for those definitions.

22.5. In early chapters of this book, we considered expansions and contractions of gases and calculated changes in thermodynamic quantities for those changes. However, we did not consider changes in surface energies, as those gases changed their surface areas. Why not?

22.6. Since energy is given off as small droplets coalesce into larger ones, maybe we can use that coalescence to perform useful work. Let's try a test case.

How much does the temperature change if two 1.00-nm-radius water droplets at 20.0°C coalesce into a single droplet? The surface tension of water is 72.75 erg/cm^2.

22.7. Approximate the surface tension of a liquid that a razor blade will *not* float on. Use the data in Example 22.3 to make your estimates.

22.8. A spherical soap bubble slowly decreases in size. Is work done on the bubble or by the bubble? Explain your answer.

22.9. **(a)** As a first approximation, raindrops can be thought of as small amounts of water in free fall, experiencing no net gravitational force. What should be their expected shape, and why?

(b) In reality, falling raindrops are distorted somewhat from their ideal shape because they are usually falling at some terminal velocity. Just considering that fact, can you predict a shape of a distorted raindrop?

22.3 Interface Effects

22.10. Explain how equation 22.9 does not violate the first law of thermodynamics.

22.11. The Laplace-Young equation can be derived in a different and incorrect way by writing the area of a sphere in terms of volume and then evaluating $\partial A/\partial V$. Why do you not get the same expression?

22.12. Show that the right side of equation 22.13, the Laplace-Young equation, has units of pressure (as required by the mathematics).

22.13. Can the evaporation of droplets be minimized by increasing the external pressure, like by pressuring region II of a system (refer to Figure 22.6) with an inert gas? Why or why not? Assume ideal behavior.

22.14. Researchers in nuclear fusion try to create tiny microspheres of gold containing deuterium-tritium mixes that they can heat to very high temperatures and pressures using focused lasers. Under such conditions, fusion of the nuclei can occur. Does the Laplace-Young equation suggest that smaller or larger microspheres would be better targets? Comment on whether this supports or detracts from the possibility of sustained fusion under these conditions.

22.15. Determine the pressure difference on a droplet of mercury with a surface tension of 480 dyn/cm if its radius is **(a)** 1.00 mm or **(b)** 0.001 mm.

22.16. Although the text did not address the effect of temperature on the Laplace-Young equation, what is the expected effect on Δp as T increases? Does this expected effect agree with equations 22.14 and 22.15 and the behavior of γ with increasing temperature?

22.17. Redraw Figure 22.8 and draw the three surface-tension vectors that contribute to equation 22.16. Using this diagram, rationalize the form of equation 22.16 and show how the cos θ term arises.

22.18. The *Kelvin equation* is used to calculate the equilibrium vapor pressure of a droplet of radius r:

$$\ln\left(\frac{p_{\text{vapor}}}{p^{\circ}_{\text{vapor}}}\right) = \frac{2\gamma \cdot \overline{V}}{r \cdot RT}$$

where p_{vapor} is the vapor pressure of the droplet, p°_{vapor} is the vapor pressure of the bulk liquid at standard conditions (that is, 25°C), and $\overline{V}$ is the molar volume of the liquid. The variables R, T, and γ have their usual meaning.

(a) Argue that the vapor pressure of a liquid increases as the radius of the droplet decreases. What implications does this have for condensation processes (that is, a vapor forming a liquid) and for atmospheric processes like raindrop formation?

(b) Calculate the vapor of a droplet of water having a radius of 20.0 nm at 298 K. The vapor pressure of bulk water at this temperature is 23.77 mmHg.

22.19. Why are capillary rises and depressions not seen for cylinders with large radii?

22.20. What is the expected contact angle if a capillary of bore radius 0.200 mm, immersed in water at 25°, shows a capillary rise of 4.78 cm?

22.4 & 22.5 Surface Films; Solid Surfaces

22.21. Show that 1 dyn/cm^2 equals 1×10^{-6} bar.

22.22. *Silicones* are polymers of silicon and oxygen chains, with organic side groups attached to the silicons. They have many useful properties and are extensively used in society. Although they have very, very low vapor pressures, they do have vapor pressures. They also have very low surface energies. Comment on the potential for silicone's presence on any real surface.

22.23. Rationalize the presence of R, the ideal gas law constant, in equation 22.21.

22.24. Atoms on a planar surface have different interatomic distances depending on the Miller indices of the exposed surface plane. NaCl has a face-centered cubic lattice with a lattice parameter of 5.640 Å. What are the closest Na^+–Na^+ distances for a surface made by **(a)** the (100) plane; **(b)** the (110) plane; and **(c)** the (111) plane?

22.25. Atoms on a planar surface have different interatomic distances depending on the Miller indices of the exposed plane. In a cubic crystal, what plane or planes have the atoms closest together?

22.26. Define the term *clean* as applied to solid surfaces. Why are clean surfaces so difficult to obtain?

22.27. From the (limited) data in Table 22.2, is there a trend for the relationship between the surface energy of ionic compounds and the magnitudes of the charges on the ions?

22.28. A china cup breaks when the ionic or covalent bonds are broken due to shock, stress, or some other influence. Even if such a cup were broken into two simple pieces, just putting the pieces back together will not make the bonds re-form. Why? We need things like glue because of this phenomenon.

22.29. Satellites in space often suffer from vacuum welding, in which two metal parts in contact tend to stick together more than expected over a period of time. Why does this phenomenon occur in space and not on Earth?

22.30. Calculate the number of gas atoms or molecules per cubic centimeter at 273 K if the pressure is 1.00×10^{-8} torr.

22.31. If an oil-filled rotary vacuum pump reaches an ultimate vacuum of 1.0×10^{-4} torr, how long does it take a surface exposed to that pressure to build up a monolayer of adsorbed molecules?

22.32. How many langmuirs is exposure to 1.00 bar for one second equal to? Does the concept of exposure hold at this magnitude? Why or why not?

22.6 Coverage; Catalysis

22.33. Are the following processes examples of homogeneous or heterogeneous catalysis? **(a)** Hydrolysis of immiscible ethyl acetate (ℓ) in an aqueous basic solution. **(b)** Conversion of NO_x gases to N_2 and O_2 by platinum metal. **(c)** Decomposition of atmospheric ozone by NO gas. **(d)** Oxidation of ethyl alcohol, C_2H_5OH, by the enzyme alcohol dehydrogenase, ADH, to acetaldehyde in the body. **(e)** Solid-state conversion of C (graphite) to C (diamond) by transition metal additives at high pressure.

22.34. Derive equation 22.27 from equation 22.26.

22.35. Early attempts to coat metals with Teflon, poly(tetrafluoroethylene), resulted in a polymer layer that peeled off the surface easily. Later attempts gave coatings that were much more durable. What type of adsorption processes are being manifested in either situation? What technical problem had to be solved in order to develop durable coatings?

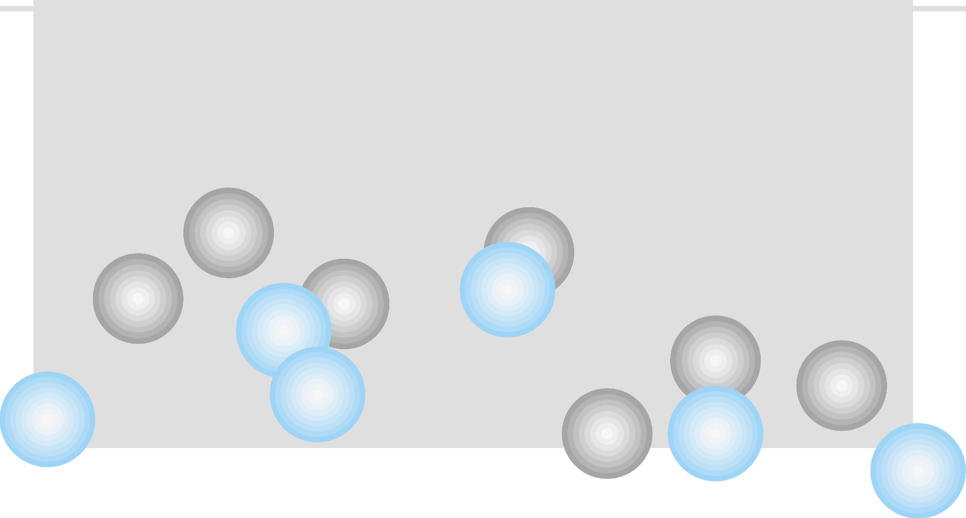
22.36. At about 450 K, carbon monoxide has the following coverages on platinum at the given pressures:

Coverage	Pressure (torr)
0.25	1.5×10^{-8}
0.45	7.0×10^{-8}
0.65	3.5×10^{-7}
0.72	8.7×10^{-7}
0.78	1.9×10^{-6}
0.82	6.8×10^{-6}

Show that this data follows a Langmuir isotherm. What is the equilibrium constant for the adsorption process?

22.37. The individual catalysis steps occurring at a surface leave out the energy of the desorption of products. Argue that this step, of necessity, should occur with very little change in energy.

Appendixes



Appendix 1 Useful Integrals

Indefinite Integrals*

$$\int \sin bx \cos bx \, dx = \frac{1}{b} \sin^2 bx$$

$$\int \sin ax \cdot \sin bx \, dx = \frac{\sin (a-b)\, x}{2\,(a-b)} + \frac{\sin (a+b)\, x}{2\,(a+b)}$$

$$\int \sin^2 bx \, dx = \frac{x}{2} - \frac{1}{4b} \sin (2bx)$$

$$\int \cos^2 bx \, dx = \frac{x}{2} + \frac{1}{4b} \sin (2bx)$$

$$\int \sin^3 bx \, dx = -\frac{1}{3b} \cos bx(\sin^2 bx + 2)$$

$$\int x \sin^2 bx \, dx = \frac{x^2}{4} - \frac{x}{4b} \sin (2bx) - \frac{1}{8b^3} \cos (2bx)$$

$$\int x \cos^2 bx \, dx = \frac{1}{b^2} \cos bx + \frac{x}{b} \sin bx$$

$$\int x^2 \sin^2 bx \, dx = \frac{x^3}{6} - \left(\frac{x^2}{4b} - \frac{1}{8b^2}\right) \sin 2bx - \frac{x}{4b^2} \cos 2bx$$

$$\int e^{bx} \, dx = \frac{1}{b} e^{bx}$$

$$\int x e^{bx} \, dx = e^{bx} \cdot \frac{1}{b^2}(bx - 1)$$

---

*Each expression must be evaluated at particular limits, typically determined by the situation under consideration.

$$\int x^2 e^{bx}\,dx = e^{bx}\left(\frac{x^2}{b} - \frac{2x}{b^2} + \frac{2}{b^3}\right)$$

$$\int x^m e^{bx}\,dx = e^{bx}\sum_{k=0}^{m}(-1)^k\,\frac{m!\cdot x^{m-k}}{(m-k)!\cdot b^{k+1}}$$

Definite Integrals[†]

$$\int_0^\infty e^{-bx^2}\,dx = \frac{1}{2}\left(\frac{\pi}{b}\right)^{1/2}$$

$$\int_0^\infty xe^{-bx^2}\,dx = \frac{1}{2}b$$

$$\int_0^\infty x^n e^{-bx}\,dx = \frac{n!}{b^{n+1}}, \qquad n \neq -1,\ b > 0$$

$$\int_{-\infty}^\infty x^2 e^{-bx^2}\,dx = \frac{1}{2}\left(\frac{\pi}{b^3}\right)^{1/2}$$

$$\int_0^\infty x^{2n} e^{-bx^2}\,dx = \frac{1\cdot 3\cdot 5\cdot\cdots\cdot(2n-1)}{2^{n+1}\cdot b^n}\cdot\sqrt{\frac{\pi}{b}}$$

[†] Each expression must be evaluated at the limits specified on the integral.

Appendix 2 Thermodynamic Properties of Various Substances

Compound	$\Delta_f H°$ (at 298 K, in kJ/mol)	$\Delta_f G°$ (at 298 K, in kJ/mol)	$S°$ [at 298 K, in J/(mol·K)]
Ag (s)	0	0	42.55
AgBr (s)	−100.37	−96.90	107.11
AgCl (s)	−127.01	−109.80	96.25
Al (s)	0	0	28.30
Al_2O_3 (s)	−1675.7	−1582.3	50.92
Ar (g)	0	0	154.84
Au (s)	0	0	47.32
$BaSO_4$ (s)	−1473.19	−1362.3	132.2
Bi (s)	0	0	56.53
Br_2 (ℓ)	0	0	152.21
C (s, diamond)	1.897	2.90	2.377
C (s, graphite)	0	0	5.69
CCl_4 (ℓ)	−128.4	−62.6	214.39
CH_2O (g)	−115.90	−109.9	218.95
$CH_3COOC_2H_5$ (ℓ)	−480.57	−332.7	259.4
CH_3COOH (ℓ)	−483.52	−390.2	158.0
CH_3OH (ℓ)	−238.4	−166.8	127.19
CH_4 (g)	−74.87	−50.8	188.66
CO (g)	−110.5	−137.16	197.66
CO_2 (g)	−393.51	−394.35	213.785
CO_3^{2-} (aq), 1 M	−413.8	−386.0	117.6
C_2H_5OH (ℓ)	−277.0	−174.2	159.86
C_2H_6 (g)	−83.8	−32.8	229.1
C_6H_{12} (ℓ)	−157.7	26.7	203.89
$C_6H_{12}O_6$ (s)	−1277	−910.4	209.19
C_6H_{14} (ℓ)	−198.7	−3.8	296.06
$C_6H_5CH_3$ (ℓ)	12.0	113.8	220.96
C_6H_5COOH (s)	−384.8	−245.3	165.71
C_6H_6 (ℓ)	48.95	124.4	173.26
$C_{10}H_8$ (s)	77.0	201.0	217.59
$C_{12}H_{22}O_{11}$ (s)	−2221.2	−1544.7	392.40
Ca (s)	0	0	41.59
Ca^{2+} (aq), 1 M	−542.83	−553.54	−53.1
$CaCl_2$ (s)	−795.80	−748.1	104.62
$CaCO_3$ (s, arag)	−1207.1	−1127.8	92.9
$CaCO_3$ (s, calc)	−1206.9	−1128.8	88.7
Cl (g)	121.30	105.3	165.19
Cl^- (aq), 1 M	−167.2	−131.3	56.4
Cl_2 (g)	0	0	223.08
Cr (s)	0	0	23.62
Cr_2O_3 (s)	−1134.70	105.3	80.65
Cs (s)	0	0	85.15
Cu (s)	0	0	33.17
D_2 (g)	0	0	144.96
D_2O (ℓ)	−249.20	−234.54	198.34
F^- (aq), 1 M	−332.63	−278.8	−13.8
F_2 (g)	0	0	202.791
Fe (s)	0	0	27.3
$Fe_2(SO_4)_3$ (s)	−2583.00	−2262.7	307.46

Compound	$\Delta_f H°$ (at 298 K, in kJ/mol)	$\Delta_f G°$ (at 298 K, in kJ/mol)	$S°$ [at 298 K, in J/(mol·K)]
Fe_2O_3 (s)	−825.5	−743.5	87.4
Ga (s)	0	0	40.83
H^+ (aq), 1 M	0	0	0
HBr (g)	−36.29	−53.51	198.70
HCl (g)	−92.31	−95.30	186.90
HCO_3^- (aq), 1 M	−691.99	−586.85	91.2
HD (g)	0.32	−1.463	143.80
HF (g)	−273.30	−274.6	173.779
HI (g)	26.5	1.7	114.7
HNO_2 (g)	−76.73	−41.9	249.41
HNO_3 (g)	−134.31	−73.94	266.39
HSO_4^- (aq), 1 M	−909.27	−744.63	20.1
H_2 (g)	0	0	130.68
H_2O (g)	−241.8	−228.61	188.83
H_2O (ℓ)	−285.83	−237.14	69.91
H_2O (s)	−292.72	—	—
He (g)	0	0	126.04
Hg (ℓ)	0	0	75.90
Hg_2Cl_2 (s)	−265.37	−210.5	191.6
I (g)	106.76	70.18	180.787
I_2 (s)	0	0	116.14
K (s)	0	0	64.63
KBr (s)	−393.8	−380.7	95.9
KCl (s)	−436.5	−408.5	82.6
KF (s)	−567.3	−537.8	66.6
KI (s)	−327.9	−324.9	106.3
Li (s)	0	0	29.09
Li^+ (aq), 1 M	−278.49	−293.30	13.4
LiBr (s)	−351.2	−342.0	74.3
LiCl (s)	−408.27	−372.2	59.31
LiF (s)	−616.0	−587.7	35.7
LiI (s)	−270.4	−270.3	86.8
Mg (s)	0	0	32.67
Mg^{2+} (aq), 1 M	−466.85	−454.8	−138.1
MgO (s)	−601.60	−568.9	26.95
NH_3 (g)	−45.94	−16.4	192.77
NO (g)	90.29	86.60	210.76
NO_2 (g)	33.10	51.30	240.04
NO_3^- (aq), 1 M	−207.36	−111.34	146.4
N_2 (g)	0	0	191.609
N_2O (g)	82.05	104.2	219.96
N_2O_4 (g)	9.08	97.79	304.38
N_2O_5 (g)	11.30	118.0	346.55
Na (s)	0	0	153.718
Na^+ (aq), 1 M	−240.12	−261.88	59.1
NaBr (s)	−361.1	−349.0	86.8
NaCl (s)	−385.9	−365.7	95.06
NaF (s)	−576.6	−546.3	51.1
NaI (s)	−287.8	−286.1	—
$NaHCO_3$ (s)	−950.81	−851.0	101.7
NaN_3 (s)	21.71	93.76	96.86
Na_2CO_3 (s)	−1130.77	−1048.01	138.79

Compound	$\Delta_f H°$ (at 298 K, in kJ/mol)	$\Delta_f G°$ (at 298 K, in kJ/mol)	$S°$ [at 298 K, in J/(mol·K)]
Na_2O (s)	−417.98	−379.1	75.04
Na_2SO_4 (s)	−331.64	−303.50	35.89
Ne (g)	0	0	146.328
Ni (s)	0	0	29.87
O_2 (g)	0	0	205.14
O_3 (g)	142.67	163.2	238.92
OH^- (aq), 1 M	−229.99	−157.28	−10.75
PH_3 (g)	22.89	30.9	210.24
P_4 (s)	0	0	41.08
Pb (s)	0	0	64.78
$PbCl_2$ (s)	−359.41	−314.1	135.98
PbO_2 (s)	−274.47	−215.4	71.78
$PbSO_4$ (s)	−919.97	−813.20	148.50
Pt (s)	0	0	25.86
Rb (s)	0	0	76.78
S (s)	0	0	32.054
SO_2 (g)	−296.81	−300.13	248.223
SO_3 (g)	−395.77	−371.02	256.77
SO_3 (ℓ)	−438	−368	95.6
SO_4^{2-} (aq), 1 M	−909.3	−744.6	20.1
Si (s)	0	0	18.82
U (s)	0	0	50.20
UF_6 (s)	−2197.0	−2068.6	227.6
UO_2 (s)	−1085.0	−1031.8	77.03
Xe (g)	0	0	169.68
Zn (s)	0	0	41.6
Zn^{2+} (aq), 1 M	−153.89	−147.03	−112.1
$ZnCl_2$ (s)	−415.05	−369.45	111.46

Source: Data from National Institute of Standards and Technology's Chemistry Webbook (available online at webbook.nist.gov/chemistry); D. R. Lide, ed., *CRC Handbook of Chemistry and Physics,* 82nd ed., CRC Press, Boca Raton, Fla., 2001; J. A. Dean, ed., *Lange's Handbook of Chemistry,* 14th ed., McGraw-Hill, New York, 1992.

Appendix 3 Character Tables

The letters in the final column indicate the irreducible representations of vibrations (x, y, and z labels) and rotations (R_x, R_y, and R_z labels) for molecules having that symmetry. Degeneracies are indicated by more than one label in parentheses. More than one label but without parentheses indicates that degeneracy will not necessarily exist (see, for example, the C_{2h} point group).

C_1	E	
A	1	all

C_s (≡ C_{1h})	E	σ_h	
A'	1	1	$x, y, R_z, x^2, y^2, z^2, xy$
A''	1	−1	z, R_x, R_y, yz, xz

C_i (≡ S_2)	E	i	
A_g	1	1	R_x, R_y, R_z, all second-order functions
A_u	1	−1	x, y, z

C_2	E	C_2	
A	1	1	$z, R_z, x^2, y^2, z^2, xy$
B	1	−1	x, y, R_x, R_y, yz, xz

C_3	E	C_3	C_3^2	$\epsilon = e^{2\pi i/3}$
A	1	1	1	$z, R_z, x^2 + y^2, z^2$
E	1	ϵ	ϵ^*	$(x, y)(R_x, R_y)(x^2 - y^2, xy)(xz, yz)$
	1	ϵ^*	ϵ	

C_4	E	C_4	C_2	C_4^3	
A	1	1	1	1	$z, R_z, x^2 + y^2, z^2$
B	1	−1	1	−1	$x^2 - y^2, xy$
E	1	i	−1	$-i$	$(x, y)(R_x, R_y)(xz, yz)$
	1	$-i$	1	i	

D_2	E	C_2	C_2'	C_2''	
A	1	1	1	1	x^2, y^2, z^2
B_1	1	1	−1	−1	z, R_z, xy
B_2	1	−1	1	−1	y, R_y, xz
B_3	1	−1	−1	1	x, R_x, yz

D_3	E	$2C_3$	$3C_2$	
A_1	1	1	1	$x^2 + y^2, z^2$
A_2	1	1	−1	z, R_z
E	2	−1	0	$(x, y)(R_x, R_y)(x^2 - y^2, xy), (xz, yz)$

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	
A_1	1	1	1	1	1	$x^2 + y^2, z^2$
A_2	1	1	1	−1	−1	z, R_z
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	$(x, y)(R_x, R_y)(xz, yz)$

S_4	E	S_4	C_2	S_4^3	
A	1	1	1	1	$R_z, x^2 + y^2, z^2$
B	1	-1	1	-1	$z, x^2 - y^2, xy$
E	1	i	-1	$-i$	$(x, y)(R_x, R_y)(xz, yz)$
	1	$-i$	-1	i	

C_{2v}	E	C_2	σ_v	σ_v'	
A_1	1	1	1	1	z, x^2, y^2, z^2
A_2	1	1	-1	-1	R_z, xy
B_1	1	-1	1	-1	x, R_y, xz
B_2	1	-1	-1	1	y, R_x, yz

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	$z, x^2 + y^2, z^2$
A_2	1	1	-1	R_z
E	2	-1	0	$(x, y)(R_x, R_y)(x^2 - y^2, xy), (xz, yz)$

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	
A_1	1	1	1	1	1	$z, x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z
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	$(x, y)(R_x, R_y)(xz, yz)$

C_{6v}	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$	
A_1	1	1	1	1	1	1	$z, x^2 + y^2, z^2$
A_2	1	1	1	1	-1	-1	R_z
B_1	1	-1	1	-1	1	-1	
B_2	1	-1	1	-1	-1	1	
E_1	2	1	-1	-2	0	0	$(x, y)(R_x, R_y)(xz, yz)$
E_2	2	-1	-1	2	0	0	$(x^2 - y^2, xy)$

C_{2h}	E	C_2	i	σ_h	
A_g	1	1	1	1	R_z, x^2, y^2, z^2, xy
B_g	1	-1	1	-1	R_x, R_y, xy, yz
A_u	1	1	-1	-1	z
B_u	1	-1	-1	1	x, y

C_{3h}	E	C_3	C_3^2	σ_h	S_3	S_3^5	$\epsilon = e^{2\pi i/3}$
A'	1	1	1	1	1	1	$R_z, x^2 + y^2, z^2$
E'	1	ϵ	ϵ^*	1	ϵ	ϵ^*	$(x, y)(x^2 - y^2, xy)$
	1	ϵ^*	ϵ	1	ϵ^*	ϵ	
A''	1	1	1	-1	-1	-1	z
E''	1	ϵ	ϵ^*	1	ϵ	ϵ^*	$(R_x, R_y)(xz, yz)$
	1	ϵ^*	ϵ	1	ϵ^*	ϵ	

D_{2h}	E	C_2	C_2'	C_2''	i	$\sigma(xy)$	$\sigma'(yz)$	$\sigma''(xz)$	
A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z, xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y, xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x, yz
A_u	1	1	1	1	−1	−1	−1	−1	
B_{1u}	1	1	−1	−1	−1	−1	1	1	z
B_{2u}	1	−1	1	−1	−1	1	−1	1	y
B_{3u}	1	−1	−1	1	−1	1	1	−1	x

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z
E'	2	−1	0	2	−1	0	$(x, y)(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1	
A_2''	1	1	−1	−1	−1	1	z
E''	2	−1	0	−2	1	0	(R_x, R_y)

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2, z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1	$x^2 - y^2$
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1	xy
E_g	2	0	−2	0	0	2	0	−2	0	0	$(R_x, R_y)(xz, yz)$
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1	
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1	
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1	
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2, z^2$
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	$(R_x, R_y)(xz, yz)$
E_{2g}	2	−1	−1	2	0	0	2	−1	−1	2	0	0	$(x^2 - y^2, xy)$
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	

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$	
A_1	1	1	1	1	1	$x^2 + y^2, z^2$
A_2	1	1	1	−1	−1	R_z
B_1	1	−1	1	1	−1	$x^2 - y^2$
B_2	1	−1	1	−1	1	z, xy
E	2	0	−2	0	0	$(x, y)(R_x, R_y)(xz, yz)$

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$	
A_{1g}	1	1	1	1	1	1	$x^2 + y^2, z^2$
A_{2g}	1	1	−1	1	1	−1	R_z
E_g	2	−1	0	2	−1	0	$(R_x, R_y)(x^2 - y^2, xy)(xz, yz)$
A_{1u}	1	1	1	−1	−1	−1	
A_{2u}	1	1	−1	−1	−1	1	z
E_u	2	−1	0	−2	1	0	(x, y)

D_{4d}	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C_2'$	$4\sigma_d$	
A_1	1	1	1	1	1	1	1	$x^2 + y^2, z^2$
A_2	1	1	1	1	1	−1	−1	R_z
B_1	1	−1	1	−1	1	1	−1	
B_2	1	−1	1	−1	1	−1	1	z
E_1	1	$\sqrt{2}$	0	$-\sqrt{2}$	−2	0	0	(x, y)
E_2	1	0	−2	0	2	0	0	$(x^2 - y^2, xy)$
E_3	1	$-\sqrt{2}$	0	$\sqrt{2}$	−2	0	0	$(R_x, R_y)(xz, yz)$

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
A_1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_2	1	1	1	−1	−1	
E	2	−1	2	0	0	$(x^2 - y^2, 2z^2 - x^2 - y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)
T_2	3	0	−1	−1	1	$(x, y, z)(xy, xz, yz)$

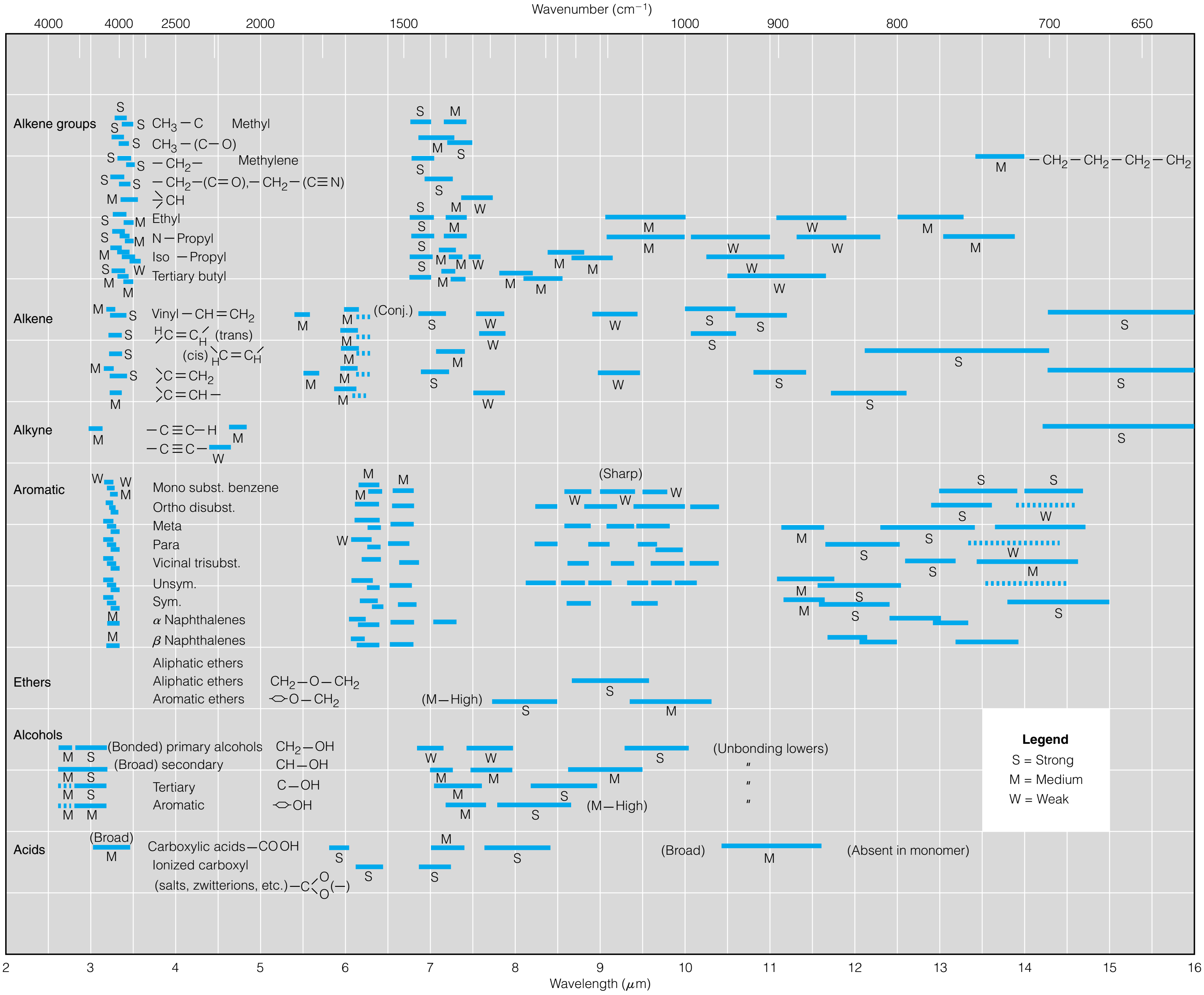
O_h	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	
E_g	2	−1	2	0	0	2	−1	2	0	0	$(x^2 - y^2, 2z^2 - x^2 - y^2)$
T_{1g}	3	0	−1	1	−1	3	0	−1	1	−1	(R_x, R_y, R_z)
T_{2g}	3	0	−1	−1	1	3	0	−1	−1	1	(xy, xz, yz)
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	2	0	0	−2	1	−2	0	0	
T_{1u}	3	0	−1	1	−1	−3	0	1	−1	1	(x, y, z)
T_{2u}	3	0	−1	−1	1	−3	0	1	1	−1	

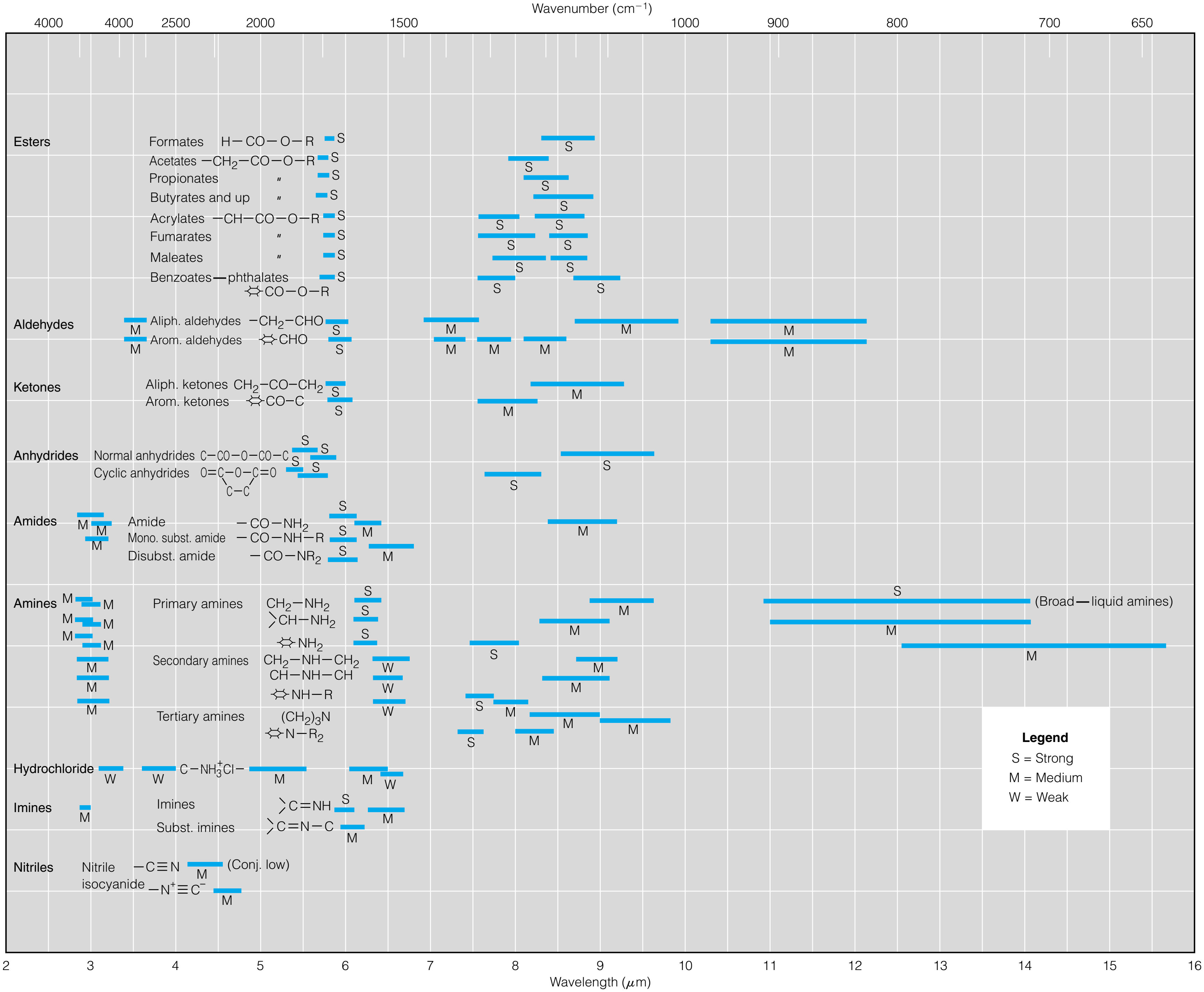
$C_{\infty v}$	E	$2C_\phi$	$\infty\sigma_v$	ϕ = any angle
Σ^+	1	1	1	$z, x^2 + y^2, z^2$
Σ^-	1	1	−1	R_z
Π	2	$2\cos\phi$	0	$(x, y)(R_x, R_y)(xz, yz)$
Δ	2	$2\cos 2\phi$	0	$(x^2 - y^2, xy)$
Φ	2	$2\cos 3\phi$	0	
$\vdots$	$\vdots$	$\vdots$	$\vdots$	
Γ_j	2	$2\cos j\phi$	0	

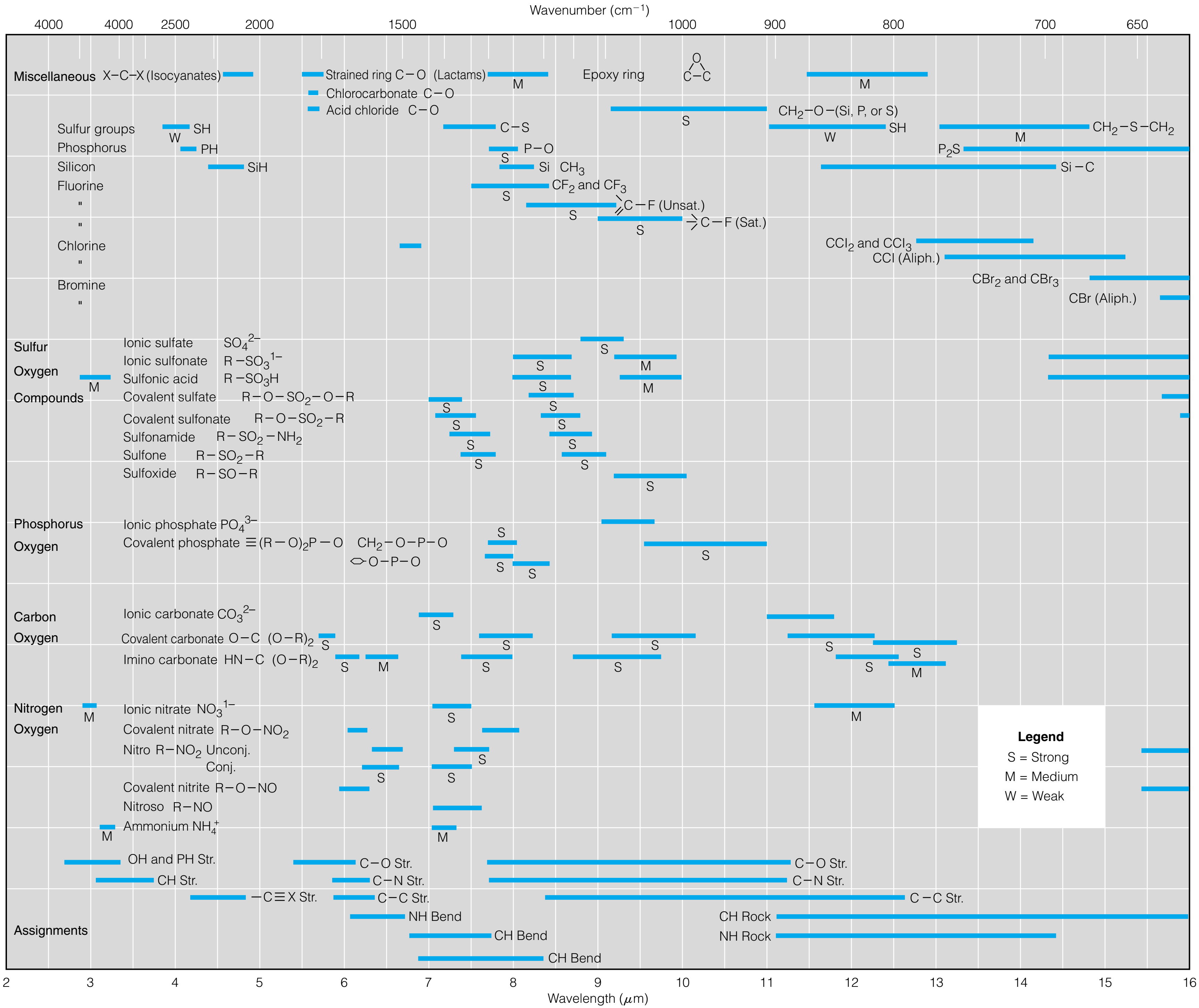
$D_{\infty h}$	E	$2C_{\phi}$	∞C_2	i	$2S_{(-\phi)}$	$\infty\sigma_v$	ϕ = any angle
Σ_g^+	1	1	1	1	1	1	x^2+y^2, z^2
Σ_g^-	1	1	−1	1	1	−1	R_z
Π_g	2	$2\cos\phi$	0	2	$-2\cos\phi$	0	$(R_x, R_y)(xz, yz)$
Δ_g	2	$2\cos 2\phi$	0	2	$2\cos 2\phi$	0	(x^2-y^2, xy)
⋮	⋮	⋮	⋮	⋮	⋮	⋮	
$\Gamma_{j,g}$	2	$2\cos j\phi$		2	$(-1)^j\cdot 2\cos j\phi$	0	
Σ_u^+	1	1	1	−1	−1	−1	z
Σ_u^-	1	1	−1	−1	−1	1	
Π_u	2	$2\cos\phi$	0	−2	$2\cos\phi$	0	(x, y)
Δ_u	2	$2\cos 2\phi$	0	−2	$2\cos 2\phi$	0	
⋮	⋮	⋮	⋮	⋮	⋮	⋮	
$\Gamma_{j,u}$	2	$2\cos j\phi$	0	−2	$-(-1)^j\cdot 2\cos j\phi$	0	

$R_h(3)$	E	C_{ϕ}	i	$S_{(-\phi)}$	σ	ϕ = any angle
$D_g^{(0)}$	1	1	1	1	1	
$D_g^{(1)}$	3	$1+2\cos\phi$	3	$1-2\cos\phi$	−1	
$D_g^{(2)}$	5	$1+2\cos\phi+2\cos 2\phi$	5	$1-2\cos\phi+2\cos 2\phi$	1	
⋮	⋮	⋮	⋮	⋮	⋮	
$D_g^{(2j+1)}$	$2j+1$	$1+\sum_{\ell=1}^{j} 2\cos\ell\phi$	$2j+1$	$1+\sum_{\ell=1}^{j}(-1)^{\ell}\cdot 2\cos\ell\phi$	$(-1)^j$	
$D_u^{(0)}$	1	1	−1	−1	−1	
$D_u^{(1)}$	3	$1+2\cos\phi$	−3	$-1+2\cos\phi$	1	
$D_u^{(2)}$	5	$1+2\cos\phi+2\cos 2\phi$	−5	$-1+2\cos\phi-2\cos 2\phi$	−1	
⋮	⋮	⋮	⋮	⋮	⋮	
$D_u^{(2j+1)}$	$2j+1$	$1+\sum_{\ell=1}^{j} 2\cos\ell\phi$	$-(2j+1)$	$-1-\sum_{\ell=1}^{j}(-1)^{\ell}\cdot 2\cos\ell\phi$	$-(-1)^j$	

Appendix 4 Infrared Correlation Tables




Wavenumber (cm⁻¹)
4000
4000
2500
2000
1500
1000
900
800
700
650
Esters
Formates H−CO−O−R
Acetates −CH₂−CO−O−R
Propionates
Butyrates and up
Acrylates −CH−CO−O−R
Fumarates
Maleates
Benzoates—phthalates
CO−O−R
Aldehydes
Aliph. aldehydes −CH₂−CHO
Arom. aldehydes CHO
Ketones
Aliph. ketones CH₂−CO−CH₂
Arom. ketones CO−C
Anhydrides
Normal anhydrides C−CO−O−CO−C
Cyclic anhydrides O=C−O−C=O C−C
Amides
Amide −CO−NH₂
Mono. subst. amide −CO−NH−R
Disubst. amide −CO−NR₂
Amines
Primary amines CH₂−NH₂
CH−NH₂
NH₂
Secondary amines CH₂−NH−CH₂
CH−NH−CH
NH−R
Tertiary amines (CH₂)₃N
N−R₂
(Broad—liquid amines)
Hydrochloride
C−NH₃⁺Cl⁻
Imines
Imines C=NH
Subst. imines C=N−C
Nitriles
Nitrile −C≡N
(Conj. low)
isocyanide −N⁺≡C⁻
S
M
W
Legend
S = Strong
M = Medium
W = Weak
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
Wavelength (μm)



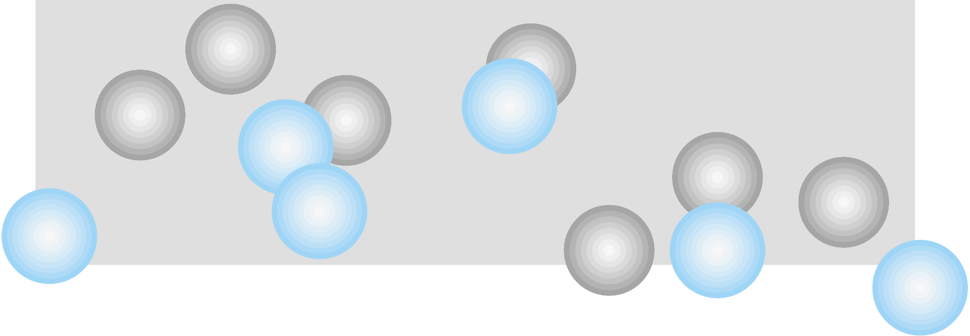
Source: D. R. Lide, ed., *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, Fla., 2001. Reprinted with permission.

Appendix 5 Nuclear Properties

Nucleus	Spin, I	Nuclear g factor, g_N
$^{1}\mathrm{H}$	$\frac{1}{2}$	5.586
$^{2}\mathrm{H}$	1	0.857
$^{3}\mathrm{He}$	$\frac{1}{2}$	−4.2552
$^{6}\mathrm{Li}$	1	0.8220
$^{7}\mathrm{Li}$	$\frac{3}{2}$	2.1709
$^{11}\mathrm{B}$	$\frac{3}{2}$	1.7923
$^{13}\mathrm{C}$	$\frac{1}{2}$	1.405
$^{14}\mathrm{C}$	0	
$^{14}\mathrm{N}$	1	0.40375
$^{15}\mathrm{N}$	$\frac{1}{2}$	−0.5662
$^{16}\mathrm{O}$	0	
$^{17}\mathrm{O}$	$\frac{5}{2}$	−0.7575
$^{19}\mathrm{F}$	$\frac{1}{2}$	5.2567
$^{23}\mathrm{Na}$	$\frac{3}{2}$	1.4783
$^{25}\mathrm{Mg}$	$\frac{5}{2}$	−0.3422
$^{27}\mathrm{Al}$	$\frac{5}{2}$	1.457
$^{28}\mathrm{Si}$	0	
$^{29}\mathrm{Si}$	$\frac{1}{2}$	−1.1105
$^{31}\mathrm{P}$	$\frac{1}{2}$	2.2634
$^{32}\mathrm{S}$	0	
$^{33}\mathrm{S}$	$\frac{3}{2}$	0.429
$^{35}\mathrm{Cl}$	$\frac{3}{2}$	0.5479
$^{37}\mathrm{Cl}$	$\frac{3}{2}$	0.4560
$^{39}\mathrm{K}$	$\frac{3}{2}$	0.26098
$^{42}\mathrm{K}$	2	NA
$^{43}\mathrm{Ca}$	$\frac{7}{2}$	−0.3763
$^{47}\mathrm{Ti}$	$\frac{5}{2}$	−0.3154
$^{49}\mathrm{Ti}$	$\frac{7}{2}$	−0.31547
$^{51}\mathrm{V}$	$\frac{7}{2}$	1.471
$^{53}\mathrm{Cr}$	$\frac{3}{2}$	−0.3163
$^{55}\mathrm{Mn}$	$\frac{5}{2}$	1.3875
$^{67}\mathrm{Zn}$	$\frac{5}{2}$	0.3502
$^{77}\mathrm{Se}$	$\frac{1}{2}$	1.068
$^{81}\mathrm{Br}$	$\frac{3}{2}$	1.5180
$^{87}\mathrm{Rb}$	$\frac{3}{2}$	1.8337
$^{87}\mathrm{Sr}$	$\frac{9}{2}$	−0.24289
$^{95}\mathrm{Mo}$	$\frac{5}{2}$	−0.3654
$^{109}\mathrm{Ag}$	1	−0.1305
$^{111}\mathrm{Cd}$	$\frac{1}{2}$	−1.1900
$^{125}\mathrm{Te}$	$\frac{1}{2}$	−1.7744
$^{127}\mathrm{I}$	$\frac{5}{2}$	1.1236
$^{133}\mathrm{Cs}$	$\frac{7}{2}$	0.7368
$^{135}\mathrm{Ba}$	$\frac{3}{2}$	0.5581
$^{137}\mathrm{Ba}$	$\frac{3}{2}$	0.6243
$^{183}\mathrm{W}$	$\frac{1}{2}$	0.2338
$^{195}\mathrm{Pt}$	$\frac{1}{2}$	1.204
$^{201}\mathrm{Hg}$	$\frac{1}{2}$	−1.1166
$^{238}\mathrm{U}$	0	

Source: G.W.C. Kaye, T. H. Laby, *Tables of Physical and Chemical Constants,* 15th ed., Longman/Wiley, New York, 1986.

Answers to Selected Exercises



Chapter 1

1.2. A system is a part of the universe under observation. A closed system is a system that does not allow for transfer of matter to or from the surroundings. Energy, however, can transfer between surroundings and a closed system.

1.3. **(a)** 1.256×10^4 cm^3 **(b)** 318 K **(c)** 1.069×10^5 Pa **(d)** 1.64 bar **(e)** 125 cm^3 **(f)** −268.9°C **(g)** 0.2575 bar

1.4. **(a)** 0°C is the higher temperature. **(b)** 300 K **(c)** −20°C

1.6. $F(T) = 0.164$ L·atm; $V \approx 0.164$ L.

1.7. $F(p) = 1.04 \times 10^{-4}\ \frac{\text{L}}{\text{K}}$; $T \approx 643$ K.

1.12. **(a)** $p_{\text{tot}} = 1.25$ atm **(b)** $p_{\text{He}} = 0.250$ atm, $p_{\text{Ne}} = 0.100$ atm **(c)** $x_{\text{He}} = 0.200$, $x_{\text{Ne}} = 0.800$

1.13. $p_{N_2} = 11.8$ lb/in^2, $p_{O_2} = 2.94$ lb/in^2

1.14. 0.0626 g CO_2 per cm^3

1.15. **(a)** 5 and 5 **(b)** 25 and 55 **(c)** −0.28 and −0.07, respectively

1.16. **(a)** $3y^2 - \dfrac{y^2z^3}{w}$ **(b)** $\dfrac{3w^2z^3}{32y} + \dfrac{xy^2z^3}{w^2}$
(c) $6xy - \dfrac{w^3z^3}{32y^2} - \dfrac{xyz^3}{w}$ **(d)** $-\dfrac{3y^2z^2}{w}$

1.17. **(a)** $-\dfrac{nRT}{p^2}$ **(b)** $\dfrac{RT}{p}$ **(c)** $\dfrac{p}{nR}$ **(d)** $\dfrac{nR}{V}$ **(e)** $\dfrac{RT}{V}$

1.18. R is a constant, not a variable.

1.19. $\left[\dfrac{\partial}{\partial p}\left(\dfrac{\partial T}{\partial V}\right)_{n,p}\right]_{n,V}$ or $\left[\dfrac{\partial}{\partial V}\left(\dfrac{\partial T}{\partial p}\right)_{n,V}\right]_{n,p}$

1.21. $T_B(CO_2) = 1026$ K, $T_B(O_2) = 521$ K, $T_B(N_2) = 433$ K

1.23. Units on C are L^2; units on C' are L/atm (for molar quantities).

1.25. In order of higher to lower predicted ideality: He, H_2, Ne, N_2, O_2, Ar, CH_4, CO_2

1.26. $a = 2.135 \times 10^5$ bar·cm^6/mol^2. The cm^6 unit comes from the fact that 1 L = 1000 cm^3, and there is an L^2 term in the original unit for a.

1.27. Under "normal" conditions of about 1 atm pressure and 25°C, V(gas) is approximately 24,500 cm^3. Therefore, the B/V term is about 6.1×10^{-4} for H_2, increasing its compressibility by about 0.06%. For H_2O, the compressibility is decreased by about 4.6%, an easily noticeable deviation from ideality.

1.30. Nitrogen's Boyle temperature is very close to room temperature, implying that its second virial coefficient B is close to zero. Therefore, N_2 would be expected to act close to ideally at room temperature.

1.32. $\left(\dfrac{\partial p}{\partial p}\right)_T = -\dfrac{\left(\dfrac{\partial T}{\partial p}\right)_p}{\left(\dfrac{\partial T}{\partial p}\right)_p}$, according to the cyclic rule. However, it makes no sense to take the derivative with respect to a variable being held constant, so no useful information can be obtained from this expression. The original expression is also mathematically useless, since we typically must find the variation in p with respect to variables other than itself.

1.33. κ has units 1/(pressure), like 1/atm or 1/bar. α has units 1/(temp), or 1/K.

Chapter 2

2.1. **(a)** 900 J **(b)** 640 J

2.3. 0.932 L·atm or 94.4 J

2.4. −3.345 L·atm or −338.9 J

2.6. $c = 0.18$ J/(g·°C)

2.8. Final temperature = 24.4°C

2.9. Approximately 1070 drops of the mass are required to raise the temperature by 1.00°C.

2.13. Equation 2.10 is applicable to isolated systems (no transfer of matter or energy). Equation 2.11 is applicable to closed systems, which allow a transfer of energy between system and surroundings.

2.14. $\Delta U = -70.7$ J

2.15. $w = +5180$ J

2.16. $w = -5705$ J (reversible), $w = -912$ J (irreversible). More work is obtained from the reversible expansion.

2.20. **(a)** $w_{\text{tot}} = 0$ **(b)** $\Delta U = 0$

2.21. **(a)** $p_{\text{final}} = 242$ atm **(b)** $w = 0$, $q = 1.44 \times 10^6$ J, $\Delta U = 1.44 \times 10^6$ J

2.22. When $q = -w$, $\Delta U = 0$ even if final conditions aren't the same as initial conditions.

2.23. $w = +2690$ J, $q = -1270$ J, $\Delta U = 1420$ J, $\Delta H = +1420$ J

2.24. $\Delta H = 2260$ J, $w = -172$ J, $\Delta U = 2088$ J

2.26. $\Delta U = -4450$ J, $p_{\text{final}} \approx 714$ atm

2.27. The units should be J/K, J/K^2, and J·K, respectively.

2.33. T(He) ≈ 36K (compared to 40 K measured experimentally), $T(H_2) \approx 224$ K (compared to 202 K measured experimentally).

2.39. Process is adiabatic: $w = -107$ J, $\Delta U = -107$ J

2.40. $T_f = 186$°C

2.44. The temperature decreases to about 55.0% of its original temperature.

2.45. $\Delta H = 333.5$ J, $\Delta U = 333.491$ J ≈ 333.5 J (4 sig figs). Even in the case of H_2O, which experiences a 9% change in volume upon melting, the difference between ΔH and ΔU is negligible for the solid-liquid phase change.

2.46. The system does 0.165 J of work.

2.48. 6.777 g of ice can be melted.

2.55. $q = 31723$ J, $\Delta U = -31723$ J, $w = 0$, $\Delta H = -31735$ J

2.56. $q = 31723$ J, $\Delta H = -31723$ J, $w = 0$, $\Delta U = -31711$ J

2.57. $\Delta H\,(-492.9$ KJ$) = -285.94$ kJ, not much different than ΔH (25°C).

Chapter 3

3.1. **(a)** spontaneous **(b)** not spontaneous **(c)** spontaneous **(d)** not spontaneous **(e)** spontaneous **(f)** spontaneous **(g)** not spontaneous

3.3. $e = 0.267$

3.4. The individual steps must also be carried out under the proper conditions (i.e., reversible & adiabatic, or reversible & isothermal). If they are, then according to the data, $e = 0.303$.

3.5. $T_{\text{low}} = -36$°C

3.6. $e = 0.268$

3.12. $\Delta S = 74.5$ J/K

3.14. $\Delta S = 23.5$ J/K

3.15. $\Delta S = 100.9$ J/K

3.16. Greater than 0.368 J/K

3.18. ΔS equals zero if the process is reversible. However, in most cases, release of compressed gas is irreversible, so the change in entropy should be greater than zero.

3.22. $\Delta S_{\text{mix}} = 4.6$ J/K

3.23. $\Delta S_{\text{mix}} = 2.20$ J/K, $\Delta S_{\text{expansion}} = 3.72$ J/K; $\Delta S_{\text{total}} = 5.92$ J/K.

3.34. From lowest to highest entropy: $C_{\text{dia}} < C_{\text{gra}} < \text{Si} < \text{Fe} < \text{NaCl} < \text{BaSO}_4$

3.36. **(a)** -163.29 J/K **(b)** -44.24 J/K **(c)** -1074.1 J/K

3.39. The difference between the two values of entropy change is 118.87 J/K. The difference is due to the phase of the product, H_2O.

3.40. $\Delta S = 37.5$ J/K

3.41. $\Delta S = 9.09 \times 10^5$ J/K

Chapter 4

4.8. Since ΔA is less than or equal to the maximum amount of work the system can do, calculate work for the given conditions and recognize that ΔA must be less than that, since the process is not reversible: $\Delta A < 517$ J.

4.9. The reaction can do up to 237.17 kJ per mole of H_2O reacted.

4.10. $\Delta A = -536$ J

4.11. $w = -15{,}700$ J, $q = 15{,}700$ J, $\Delta U = 0$, $\Delta H = 0$, $\Delta A = -15{,}700$ J, $\Delta S = 57.5$ J/K

4.12. -97.7 kJ

4.13. $+2.3$ kJ and $+138.3$ kJ

4.17. $\Delta A = 0$ (because it's a state function)

4.23. **(a)** yes **(b)** yes **(c)** yes **(d)** yes **(e)** no

4.28. ΔU should change by approximately 4460 J.

4.34. 38.5 J/K

4.36. slope $= \Delta H$

4.37. $\Delta G = -967$ J

4.42. All are intensive variables.

4.44. **(a)** -1.91×10^3 J **(b)** -5.74×10^3 J

4.45. -29.7 J

Chapter 5

5.5. The minimum ξ is 0. The maximum ξ is 0.169 mol, as determined by the limiting reagent HCl.

5.6. **(a)** $\xi = 1.5$ mol **(b)** ξ cannot equal 3 in this case, because H_2 will act as a limiting reagent at $\xi = 1.66$ mol.

5.9. False. $p°$ is the standard pressure, defined as 1 atm or 1 bar.

5.10. $\Delta_{rxn}G° = -514.38$ kJ; $\Delta_{rxn}G = -489.49$ kJ

5.11. **(b)** $\Delta G° = -68$ kJ **(c)** $K = 8.2 \times 10^{11}$

5.12. The system would not necessarily be at equilibrium, because the p_i or p_j values in equation 5.9 now have different values. Only if there were the same number of moles on either side of the chemical reaction would these partial pressures cancel mathematically and the equilibrium constants have the same value.

5.14. **(a)** $\Delta G° = -32.8$ kJ **(b)** $\Delta_{rxn}G = -29.4$ kJ

5.15. ΔG will be zero when all partial pressures are approximately 1.29×10^{-3} atm.

5.16. $p(H_2) = 0.4167$ atm, $p(D_2) = 0.0167$ atm, $p(HD) = 0.1667$ atm, $\xi = 0.0833$ mol

5.18. **(a)** $K = 6.96$ **(b)** $\xi = 0.393$

5.19. $\Delta G° = 10.2$ kJ, $K = 1.63 \times 10^{-2}$

5.21. **(a)** $K = \dfrac{\dfrac{\gamma_{Pb^{+2}} \cdot m_{Pb^{+2}}}{m°}\left(\dfrac{\gamma_{Cl^-} \cdot m_{Cl^-}}{m°}\right)^2}{\dfrac{\gamma_{HNO_2} \cdot m_{HNO_2}}{m°}}$

(b) $\dfrac{\dfrac{\gamma_{H^+} \cdot m_{H^+}}{m°}\,\dfrac{\gamma_{NO_2^-} \cdot m_{NO_2^-}}{m°}}{\dfrac{\gamma_{HNO_2} \cdot m_{HNO_2}}{m°}}$ **(c)** $\dfrac{\dfrac{p_{CO_2}}{p°}}{\dfrac{\gamma_{H_2C_2O_4} \cdot m_{H_2C_2O_4}}{m°}}$

5.22. $K = 0.310$

5.23. $p \approx 1.49 \times 10^4$ atm

5.24. $K = 6.3 \times 10^{-5}$

5.25. **(a)** $\Delta G° = 10.96$ kJ **(b)** $m_{H^+} = m_{SO_4{}^{2-}} = 6.49 \times 10^{-3}$ molal, $m_{HSO_4{}^-} = 3.51 \times 10^{-3}$ molal

5.26. $\Delta H° \approx -77$ kJ

5.27. A 5-K temperature drop, to 293 K, increases K by a factor of 2. Lowering the temperature to 282 K, a drop of 16 K, increases K by a factor of 10. For $\Delta H = -20$ kJ, the temperatures necessary are 274 K and 232 K, respectively.

Chapter 6

6.1. **(a)** 1 **(b)** 2 **(c)** 4 **(d)** 2 **(e)** 2

6.3. $FeCl_2$ and $FeCl_3$ are the only chemically stable, single-component materials that can be made from iron and chlorine. Note that we are identifying single components as the compound, not the elements that make up the compound.

6.6. **(a)** The equilibrium shifts toward the liquid phase. **(b)** The equilibrium shifts to the gas phase. **(c)** The equilibrium shifts to the solid phase. **(d)** No change in phase is expected (unless there is a stabler solid allotrope or crystal form; metallic tin is one example).

6.7. By definition, every pure substance has only one normal boiling point.

6.8. $-dn_{liquid} = dn_{solid}$

6.12. $\partial\mu/\partial T = -214$ J/K

6.13. $\Delta S = 87.0$ J/mol

6.14. MP (Ni) ≈ 1452°C

6.15. MP (Pt) ≈ 3820°C

6.17. Assumptions are that ΔH and ΔV are invariant over the temperature range involved.

6.19. A pressure of ~7.3 atm will make the rhombic form of sulfur the stable phase at 100°C.

6.21. **(a)** yes **(b)** yes **(c)** no **(d)** no **(e)** no **(f)** no **(g)** no **(h)** yes

6.23. A pressure of ~7.3 atm will make the rhombic form of sulfur the stable phase at 100°C. This is very similar to the pressure predicted in equation 6.10.

6.26. The Clausius-Clapeyron equation predicts decreasing vapor pressures in the following order: *tert*-butanol (44.7 mmHg), 2-butanol (20.5 mmHg), isobutanol (13.6 mmHg), and 1-butanol (9.6 mmHg). This order is also the lowest-to-highest in normal boiling points of the isomers.

6.27. $dp/dT = 7.8 \times 10^{-6}$ bar/K, or about $\frac{6}{1000}$ mmHg per degree K

6.28. $p = 0.035$ bar

6.30. $p \approx 97$ atm, corresponding to approximately 800 m beneath the ocean surface.

6.38. Higher pressures are needed to have a stable liquid phase for a compound that sublimes under normal pressure. CO_2 is an example.

Chapter 7

7.1. Degrees of freedom = 3

7.3. There would have to be five distinct phases (for example, you could have three different solid phases).

7.7. Minimum amount of H_2O is 6.39×10^{-3} mol (0.115 g); minimum amount of CH_3OH is 3.36×10^{-2} mol (1.08 g).

7.8. $y_{H_2O} = 0.0928$; $y_{CH_3OH} = 0.907$

7.9. $a = 0.984$

7.12. Total vapor pressure equals 124.5 torr.

7.13. $p_{EtOH} = 0.0693$ torr

7.14. $x_{MeOH} = 0.669$, $x_{EtOH} = 0.331$

7.16. $y_{C_6H_{14}} = 0.608$, $y_{C_6H_{12}} = 0.392$

7.18. Equation 7.24 is written in terms of the *vapor*-phase composition, not the liquid-phase composition.

7.19. $\Delta_{mix}G = -3380$ J (for 2 mol of material), $\Delta_{mix}S = -11.5$ J/K (for 2 mol of material)

7.23. Determine the temperature of phase transition (melting, boiling) and compare it with pure components.

7.24. Benzene is poisonous and a suspected carcinogen.

7.25. Using a 50:50 mix of ethylene glycol and water lowers its freezing point to below those of the individual components.

7.26. $K = 1.23 \times 10^6$ mmHg $= 1.62 \times 10^3$ atm $= 1.64 \times 10^3$ bar

7.28. 2.4×10^3 Pa

7.29. Molarity ≈ 0.00232 M; $K \approx 2.43 \times 10^9$ Pa

7.30. **(a)** $M \approx 0.00077$ M **(b)** $K \approx 7.3 \times 10^9$ Pa **(c)** Decrease

7.33. $M \approx 5.08$ M

7.34. $x_{\text{phenol}} = 0.79$, suggesting a solubility of over 1900 g of phenol per 100 g of H_2O. The reason for this odd result is that H_2O and phenol do not form an ideal solution.

7.35. **(a)** 2.78 M **(b)** 29.7 g/100 mL, or about 1.80 M

7.39. MP (Fe, est) = 1515 K

7.45. $x_{\text{Na}} = 0.739$

7.49. BP = 101.1°C, MP = −4.0°C, $\Pi = 52.5$ bar

7.50. Δ(MP) = −9.8°C

7.53. $K_f = 8.89$°C/molal

Chapter 8

8.1. 2.50×10^{-8} C

8.2. **(a)** $F = 3.54 \times 10^{22}$ N **(b)** Charge equals 2.97×10^{17} C, which is approximately 3×10^{12} mol e^-. This mass of this many electrons is approximately 1.7×10^6 kg, 18 orders of magnitude less massive than Earth.

8.3. **(a)** Charge equals 4.98×10^{-9} C and 9.96×10^{-9} C. **(b)** $E = 312$ and 156 J/(C·m) (or V/m).

8.4. 1 C = 2.998×10^9 statcoulombs

8.5. $F = 8.24 \times 10^{-8}$ N

8.6. $w = 1.602 \times 10^{-19}$ J

8.8. **(a)** $4\,MnO_2 + 3O_2 + 2H_2O \rightarrow 4MnO_4^- + 4H^+$, $E° = -1.278$ V, $\Delta G° = 1480$ kJ **(b)** $2Cu^+ \rightarrow Cu + Cu^{2+}$, $E° = 0.368$ V, $\Delta G° = -35.5$ kJ

8.12. Only part b could provide enough energy to perform the task.

8.13. $E°$ values are shifted up or down by 0.2682 V depending on whether the calomel is used as the reduction reaction or the oxidation reaction in the cell.

8.14. **(a)** $E° = 1.401$ V, $\Delta G = -270.3$ kJ **(b)** $E° = 0.0067$ V, $\Delta G = -2.6$ kJ

8.17. $[Zn^{2+}]/[Cu^{2+}] = \sim 3210$

8.18. $E \approx 1.514$ V

8.19. **(a)** $E° = 0.00$ V **(b)** $Q = [Fe^{3+}]/[Fe^{3+}] = \frac{0.001}{0.08}$ **(c)** $E = 0.0375$ V

8.20. $K = 3.25 \times 10^{-2}$

8.23. $\Delta C_p = -n\mathcal{F}\left(2\frac{\partial E°}{\partial T} + T\frac{\partial^2 E°}{\partial T^2}\right)$

8.31. $[Cl^-] \approx 1.38 \times 10^{-6}$ M

8.33. **(a)** 0.0055 m **(b)** 0.075 m **(c)** 0.0750 m **(d)** 0.150 m

8.40. $\gamma_\pm = 0.949$, using equation 8.49

8.48. $v_i = 4.735 \times 10^{-6}$ m/s, which is over 10,000 times its radius per second

Chapter 9

9.1. $L = \frac{1}{2}m\dot{z}^2 - mgz$; $\partial m\dot{z}/\partial t = -mg$

9.2. $H = \frac{1}{2}m\dot{z}^2 + mgz$

9.4. **(a)** Newton's **(b)** Lagrange's or Hamilton's

9.6. **(a)** 459,000 cm^{-1} **(b)** 2690 cm^{-1} **(c)** 3020 cm^{-1}

9.7. The two compounds should share at least one constituent element.

9.8. This "line" corresponds to $n_1 = \infty$.

9.9. For the Lyman series, the series limit equals 109,700 cm^{-1}. For the Brackett series, the series limit equals 6856 cm^{-1}.

9.10. **(a)** 105,350 cm^{-1} **(b)** 25,720 cm^{-1} **(c)** 5334 cm^{-1}

9.12. $e/m \approx 1.71 \times 10^{11}$ C/kg (using Milliken's data from the chapter). Modern measurements give this ratio as 1.76×10^{11} C/kg.

9.13. **(a)** It takes over 7300 e^- to equal the mass of an He nucleus.

9.14. **(a)** 5.67×10^4 W/m^2 **(c)** 1420 W

9.15. $T = 65$ K, 115 K, and 205 K, respectively

9.16. 340 W

9.17. **(a)** 6.42×10^7 W/m^2 **(b)** 3.91×10^{20} W **(c)** 1.23×10^{28} J per year

9.18. **(a)** 5.55×10^6 J/m^4 **(b)** 1.06×10^7 J/m^4 **(c)** 1.11×10^3 J/m^4 **(d)** 69.4 J/m^4

9.19. **(a)** 4996 Å

9.20. **(a)** 5.12×10^{-5} J/m^4 **(b)** 90.5 J/m^4 **(c)** 497.1 J/m^4 **(d)** 47.4 J/m^4

9.22. For $T = 1000$ K, $dE = 0.101$ W/m^2

9.24. For Li, $\lambda_{\text{min}} = 428$ nm

9.25. **(a)** 1.82×10^5 m/s

9.29. $r = 8.47$, 13.2, and 19.1 Å, respectively

9.30. $E = -1.367 \times 10^{-19}$, -8.716×10^{-20}, and -6.053×10^{-20} J, respectively

9.31. $L = 4.22 \times 10^{-34}$, 5.27×10^{-34}, and 6.33×10^{-34} J·s, respectively

9.36. $\lambda_{\text{baseball}} = 1.49 \times 10^{-34}$ m; $\lambda_{e^-} = 1.64 \times 10^{-5}$ m (or 16.4 microns)

9.37. $v_{e^-} = 7.27 \times 10^6$ m/s; $v_{p^+} = 3.96 \times 10^3$ m/s

Chapter 10

10.2. Finite, continuous, single-valued, integrable

10.3. **(a)** yes **(b)** no; not bounded (Note that the fact that the function is imaginary for negative values of x is not an issue, as functions are not required to be real!) **(c)** no; not continuous **(d)** yes, if it can be normalized **(e)** no; not bounded **(f)** yes **(g)** no; not single-valued

10.4. **(a)** multiplication **(b)** addition **(c)** natural logarithm **(d)** sine **(e)** exponential function **(f)** first derivative with respect to x

10.5. **(a)** 6 **(b)** 9 **(f)** $12x^2 - 7 - 7/x^2$

10.6. **(a)** $12x^2 + 4x^{-3}$ **(b)** -2 **(c)** $\sin \frac{2\pi x}{3}$ **(d)** $\frac{1}{\sqrt{10}}$ **(e)** $-\frac{1}{45x^2y^2}$

10.7. $(-4, 5, 6)$ **(b)** $(0, 4, 1)$

10.8. **(a)** no **(b)** yes; eigenvalue $= -\frac{\pi^2}{4}$ **(c)** no **(d)** yes; eigenvalue $= -m\hbar$ **(e)** no **(f)** yes; eigenvalue $= \left(\frac{4\pi^2\hbar^2}{18m} + 0.5\right)$

10.13. $p_\phi = m\hbar$

10.14. $\Delta x_{\text{baseball}} \geq 3.80 \times 10^{-34}$ m, $\Delta x_{e^-} \geq 8.04 \times 10^{-2}$ m

10.15. $\Delta x \geq 4.71 \times 10^{-9}$ m

10.17. $\Delta t \geq 2.65 \times 10^{-12}$ s

10.18. **(a)** $P = 0.0000526$ **(b)** $P = 0.0200$ **(c)** $P = 0.0400$ **(d)** $P = 0.0200$ **(e)** $P = 0.0000526$

10.19. **(a)** $\Psi = \frac{1}{\sqrt{2\pi}} e^{im\phi}$ **(b)** $P = \frac{1}{3}$

10.28. $E = \frac{\hbar^2\pi^2}{2m}, \frac{\hbar^2\pi^2}{2m} + 0.5$

10.30. **(a)** $E = \frac{\hbar^2 K^2}{2m}$ **(b)** $E = \frac{\hbar^2 K^2}{2m} + k$ **(c)** $E = \frac{\hbar^2\pi^2}{8ma^2}$

10.33. length ≈ 5.74 Å

10.34. 4, 9, and 99 nodes, respectively

10.37. $P = 0.0200, 0.000008, 0.01998, 0.000028$

10.42. $\langle x \rangle = 0.5a$

10.43. $\langle p \rangle = 0$

10.45. $p_\phi = 3\hbar$, $\langle p_\phi \rangle = 3\hbar$

10.50. The five lowest energies are, in order, $\Psi(1, 1, 1)$, $\Psi(1, 1, 2)$, $\Psi(1, 1, 3)$, $\Psi(1, 2, 1)$, and $\Psi(2, 1, 1)$ (where the quantum numbers are listed in order of the dimensions given).

10.51. Degeneracy first appears when one of the quantum numbers equals 2 [i.e., $E(1, 1, 2) = E(1, 2, 1) = E(2, 1, 1)$]. The first appearance of "accidental" degeneracy occurs for $E(3, 3, 3) = E(5, 1, 1) = E(1, 5, 1) = E(1, 1, 5)$.

10.54. $\langle x \rangle = a/2$, $\langle y \rangle = b/2$, $\langle z \rangle = c/2$.

10.58. **(a)** 1 **(b)** 0 **(c)** $16h^2/8ma^2$ **(d)** 0 **(e)** 1 **(f)** 0 **(g)** $h^2/8m\,(1/a^2 + 1/b^2 + 1/c^2)$ **(h)** 0

Chapter 11

11.1. 335.8 N/m

11.2. $k = 1515$ N/m

11.9. **(a)** $\Delta E = 6.63 \times 10^{-34}$ J **(b)** $\lambda = 3.00 \times 10^8$ m

11.10. **(a)** $\Delta E = 3.976 \times 10^{-20}$ J **(b)** $\lambda = 5.00 \times 10^{-6}$ m **(c)** infrared region

11.11. $\nu = 4.36 \times 10^{14}$ s, $\lambda = 6.88 \times 10^{-7}$ m

11.14. $\langle p_x \rangle = 0$ for both $\Psi(0)$ and $\Psi(1)$

11.16. **(a)** zero **(b)** zero **(c)** probably not identically zero **(d)** zero **(e)** indeterminate **(f)** indeterminate; it depends on the form of the potential energy, V

11.17. $x = \pm\left[\frac{(2n + 1)h\nu}{k}\right]^{1/2}$

11.18. 9.109×10^{-31} kg versus **(a)** 9.104×10^{-31} kg, **(b)** 9.107×10^{-31} kg, **(c)** ~9.109×10^{-31} kg

11.20. **(a)** $\nu = 6.504 \times 10^{13}$ s^{-1} **(b)** 6.359×10^{13} s^{-1}

11.21. Approximately 2660 cm^{-1}

11.24. $E(0) = 0$, $E(1) = 2.68 \times 10^{-19}$ J, $E(2) = 1.07 \times 10^{-18}$ J, $E(3) = 2.41 \times 10^{-18}$ J, $E(4) = 4.28 \times 10^{-18}$ J

11.26. $\Psi(0) = \frac{1}{\sqrt{2\pi}}$, $\Psi(1) = \frac{1}{\sqrt{2\pi}}(\cos\phi + i\sin\phi)$, $\Psi(2) = \frac{1}{\sqrt{2\pi}}(\cos 2\phi + i\sin 2\phi)$, $\Psi(3) = \frac{1}{\sqrt{2\pi}}(\cos 3\phi + i\sin 3\phi)$

11.27. **(b)** $E(2) - E(1) \approx 62.1$ cm^{-1}

11.32. $\langle r \rangle$ cannot be evaluated for Y^2_{-2} because r is not a variable of the spherical harmonic.

11.34. **(a)** $E = 7.506 \times 10^{-22}$ J **(b)** $L_{\text{tot}} = 2.583 \times 10^{-34}$ J·s **(c)** The z component of the total angular momentum could be $-2\hbar$, $-1\hbar$, 0, $1\hbar$, or $2\hbar$.

11.35. **(b)** $E(2) - E(1) \approx 41.3$ cm^{-1}. (Compare with 11.27.)

11.36. $\Delta E\ (\ell = 5 \rightarrow \ell = 6) = 5.95 \times 10^{-19}$ J, equivalent to $\lambda = 334$ nm (cf. 328 nm experimentally).

11.41. $V = -4.36 \times 10^{-18}$ J

11.42. $V = -1.92 \times 10^{-57}$ J

11.49. $\ell = 4$ is not allowed for $n = 4$.

11.50. $E_H = -1312$ kJ/mol, $E_{He} = -5249$ kJ/mol.

11.51. $P = 0.68\%$ for a 1*s* electron.

11.53. Radial, angular, and total nodes respectively: **(a)** 1, 0, and 1 for Ψ_{2s} **(b)** 2, 0, and 2 for Ψ_{3s} **(c)** 1, 1, and 2 for Ψ_{3p} **(d)** 0, 3, and 3 for Ψ_{4f}.

11.57. $\Psi_{2p_x} = \dfrac{1}{4\sqrt{2}}\left(\dfrac{2Z^3}{\pi a^3}\right)^{1/2}\dfrac{Zr}{a}e^{-Zr/a}\sin\theta\cos\phi$

11.60. $\langle r\rangle = 1.5a$ for Ψ_{1s}, where $a = 0.529$ Å

Chapter 12

12.2. $\Psi(3d_{-2}) = \dfrac{1}{162}\left(\dfrac{Z^3}{\pi a^3}\right)^{1/2}\dfrac{Z^2r^2}{a^2}e^{-Zr/3a}\sin^2\theta\cdot e^{-2i\phi}\cdot\alpha$ or $\dfrac{1}{162}\left(\dfrac{Z^3}{\pi a^3}\right)^{1/2}\dfrac{Z^2r^2}{a^2}e^{-Zr/3a}\sin^2\theta\cdot e^{-2i\phi}\cdot\beta$

12.3. e^-/e^+ annihilation $= 1.637 \times 10^{-13}$ J or 9.860×10^{10} J/mol

12.4. Yes, α and β spin functions are orthogonal.

12.5. (b) $m_s = 0$; $m_s = -2, -1, 0, +1$, or $+2$; $m_s = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}$, or $+\frac{3}{2}$.

12.6. **(a)** negative **(b)** positive **(c)** negative **(d)** negative **(e)** positive

12.7.
$$\widehat{H} = -\frac{\hbar^2}{2\mu}(\nabla^2_{e1} + \nabla^2_{e2} + \nabla^2_{e3}) - \frac{3e^2}{4\pi\epsilon_0 r_1} - \frac{3e^2}{4\pi\epsilon_0 r_2} - \frac{3e^2}{4\pi\epsilon_0 r_3} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{13}} + \frac{e^2}{4\pi\epsilon_0 r_{23}}}_{\text{not separable}}$$

12.8. **(a)** $E = -5.883 \times 10^{-17}$ J **(b)** $E = -4.412 \times 10^{-17}$ J

12.11. $\Psi_{\mathrm{Li}^+} = \dfrac{1}{\sqrt{2}}[(1s_1\alpha)(1s_2\beta) - (1s_2\alpha)(1s_1\beta)]$

12.12. H has only a single electron, so there is no antisymmetry with respect to exchange to consider.

12.13. **(a)**
$$\Psi_{\mathrm{Be}} = \frac{1}{\sqrt{24}}\begin{vmatrix} 1s_1\alpha & 1s_1\beta & 2s_1\alpha & 2s_1\beta \\ 1s_2\alpha & 1s_2\beta & 2s_2\alpha & 2s_2\beta \\ 1s_3\alpha & 1s_3\beta & 2s_3\alpha & 2s_3\beta \\ 1s_4\alpha & 1s_4\beta & 2s_4\alpha & 2s_4\beta \end{vmatrix}$$

$$\Psi_{\mathrm{B}} = \frac{1}{\sqrt{120}}\begin{vmatrix} 1s_1\alpha & 1s_1\beta & 2s_1\alpha & 2s_1\beta & 2p_{x,1}\alpha \\ 1s_2\alpha & 1s_2\beta & 2s_2\alpha & 2s_2\beta & 2p_{x,2}\alpha \\ 1s_3\alpha & 1s_3\beta & 2s_3\alpha & 2s_3\beta & 2p_{x,3}\alpha \\ 1s_4\alpha & 1s_4\beta & 2s_4\alpha & 2s_4\beta & 2p_{x,4}\alpha \\ 1s_5\alpha & 1s_5\beta & 2s_5\alpha & 2s_5\beta & 2p_{x,5}\alpha \end{vmatrix}$$

(The last column could be $2p_x\beta$, or $2p_y\alpha$ or β, or $2p_z\alpha$ or β. Thus, there are six possible determinants for a B atom.) **(b)** C has six different possible determinants, as does F.

12.14. C has 720 terms in its antisymmetric wavefunction; Na has 39,916,800, and Si has 87,178,291,200 terms.

12.16. **(a)** excited **(b)** ground **(c)** excited **(d)** excited

12.17. **(a)** Li ($1s^2\ 2p^1$) will have six possible arrangements: $1s^2\ 2p_x^1\alpha$, $1s^2\ 2p_x^1\beta$, $1s^2\ 2p_y^1\alpha$, $1s^2\ 2p_y^1\beta$, $1s^2\ 2p_z^1\alpha$, and $1s^2\ 2p_z^1\beta$.

12.18. The correction to the energy won't be an exact correction even if the integral can be solved analytically because the wavefunctions in the integral are for the ideal system, not the real system.

12.19. $\langle E_{\mathrm{perturb}}\rangle = 3c/(4\alpha^2)$, where c is the anharmonicity constant.

12.20. A correction like cx^3 makes the integrand an odd function, making the numerical value of the integral exactly zero.

12.21. $a_3 = -15kma^2/(16\pi^2h^2)$

12.24. **(a)** no (unless both *A* & *B* equal zero, which is a trivial wavefunction anyway) **(b)** no **(c)** no **(d)** yes **(e)** no **(f)** no **(g)** no. Most of these trial functions do not satisfy the boundary conditions for a particle-in-a-box.

12.34. The Born-Oppenheimer approximation is more applicable to Cs_2, whose nuclei move more slowly than those in H_2.

12.35. $\Delta E = \dfrac{2(H_{11}S_{12} - H_{12})}{(1 - S_{12}^2)}$

12.40. For example, B: $(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p_x, \pi_u 2p_y)$

12.42. No, F_2^{2-} should not exist according to MO theory.

Chapter 13

13.2. **(a)** *E*, C_2 (principal axis), $4C_2'$ (perpendicular to principal axis), σ_h, $2\sigma_v$, *i*, S_2 **(b)** *E*, C_2, $2\sigma_v$ **(c)** *E*, several σ's

13.3. **(b)** C_{2v}

13.5. **(a)** Complete group **(b)** Complete group **(c)** Incomplete group: *E* missing **(d)** Incomplete group: C_3^2 (the inverse of C_3) missing

13.6. $C_2 = \begin{bmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$, $C_3 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$

13.7. **(a)** $S_n = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$ **(b)** $i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

13.8. **(a)** 4 classes, order = 4 **(b)** 8 classes, order = 8 **(c)** 12 classes, order = 24 **(d)** 3 classes, order = 4 **(e)** 2 classes, order = 2 **(f)** 5 classes, order = 24

13.10. **(a)** S_4^3, which is classed with the other S_4 symmetry operations in the T_d character table **(b)** C_2, which is its own inverse

13.11. **(a)** σ_v' **(b)** σ_h **(c)** S_6 **(d)** S_4 **(e)** C_4^3

13.12. Symmetry elements do not necessarily follow the commutative law (this is more apparent for larger groups).

13.13. Porphine has D_{2h} symmetry as a molecule; substituting metal ions for the two H's inside the porphine ring, and the symmetry becomes D_{4h}.

13.14. C_{2v}

13.17. **(a)** C_2 **(b)** D_{2d} **(c)** C_1 **(e)** C_{2v}

13.18. **(a)** C_{2v} **(b)** C_s **(c)** D_{3d} **(e)** D_{3h}

13.19. **(a)** C_{2v} **(b)** D_{3h} **(c)** C_{2v}

13.20. **(a)** $C_{\infty v}$ **(b)** C_{2v} (c) D_{3h}

13.21. **(a)** C_4H_4, C_8H_8, $C_{12}H_{12}$, and $C_{20}H_{20}$. The final Platonic solid cannot exist as a hydrocarbon. All but C_4H_4 have been synthesized by organic chemists.

13.22. **(a)** yes **(b)** yes **(c)** yes **(d)** no **(e)** no **(f)** no **(g)** no **(h)** no **(i)** yes

13.23. c, e, f, g, k, l, and m will not have permanent dipole moments.

13.24. **(a)** C_1 (i.e., only the E symmetry element is present) **(b)** Still C_s, so no longer chiral (for rules in determining chirality, consult an organic chemistry textbook)

13.30. At least one threefold (or higher) rotational axis is necessary to have an E irreducible representation.

13.31. The irreducible representations are from different point groups, and have different symmetry classes and orders. Therefore, the great orthogonality theorem does not apply.

13.32. In $C_{\infty v}$ and $D_{\infty h}$, any value of ϕ is possible for a proper or improper rotation.

13.33. $\Gamma(f \text{ orbitals in } O_h) = A_{2u} \oplus T_{1u} \oplus T_{2u}$

13.34. **(a)** Sin ϕ has E, $\sigma(xy)$, S_2 (the y-axis), and i. **(b)** Cos ϕ has E, C_2 (the y-axis), and 2σ's (the xy and the yz planes).

13.35. The symmetry elements in this case would be the same as for cos ϕ in answer 13.34b.

13.36. Either $C_{\infty v}$ or $D_{\infty h}$

13.39. **(a)** $3\,A \oplus 2B$ **(b)** $A_1 \oplus A_2 \oplus 2E$

13.40. **(a)** A_2 **(b)** $B_1 \oplus B_2 \oplus E_1$ **(c)** E' **(d)** A_{1u}

13.41. Of the first four answered above, all of the integrals of functions with those symmetry labels would be identically zero because they do not contain the all-symmetric irreducible representation (A_1 or A').

13.42. Yes, a transition can occur, because in the C_{4v} point group the combination $E \times E \times B_2$ does contain A_1.

13.43. The transition is forbidden because $D_g^{(0)} \times D_g^{(0)} \times D_u^{(1)}$ does not contain $D_g^{(1)}$.

13.44. The d orbitals have $E \oplus T_2$ irreducible representations; E is doubly degenerate and T_2 is triply degenerate.

13.51. The three closely spaced lines are the three wavefunctions that make up the triplet state (see equation 13.22).

13.55. sp^2

13.57. $2A_1' \oplus A_2'' \oplus E'$

Chapter 14

14.1. There is no rotating dipole when a linear molecule rotates about its molecular axis.

14.2. **(a)** exactly zero **(b)** exactly zero **(c)** may be nonzero **(d)** exactly zero

14.3. **(a)** 3.00×10^8 s^{-1} **(b)** 6.28×10^{12} s^{-1} **(c)** 3.798×10^{14} s^{-1} **(d)** 1.575×10^5 s^{-1}

14.4. No, it is not allowed.

14.5. $\lambda = 3.728 \times 10^{-5}$ m, $c = 3.00 \times 10^8$ m/s, $E = 5.328 \times 10^{-21}$ J

14.7. $\lambda(\mu\text{m}) \cdot \tilde{\nu} = 10{,}000$

14.8. $E = 0$, 2.58×10^{-22} J, 7.74×10^{-22} J, 1.55×10^{-21} J

14.9. **(a)** prolate symmetric top **(b)** spherical top **(c)** spherical top **(d)** asymmetric top **(e)** asymmetric top **(f)** asymmetric top **(g)** oblate symmetric top **(h)** linear

14.10. $B = 5.91 \times 10^{-24}$ J $= 0.2979$ cm^{-1}

14.11. $B(SF_6) = 1.80 \times 10^{-24}$ J, $B(UF_6) = 1.10 \times 10^{-24}$ J. The difference is due to the larger bond distances in UF_6; the S and U atoms themselves do not contribute to the moment of inertia because they are at the intersection of all symmetry elements.

14.12. $A = B = 1.015 \times 10^{-22}$ J ($= 0.196$ cm^{-1}), $C = 8.368 \times 10^{-23}$ J ($= 0.237$ cm^{-1})

14.14. $E = 0$, 1.674×10^{-22} J, 2.030×10^{-22} J, 5.021×10^{-22} J, 6.090×10^{-22} J

14.16. b, c, e, h, i, and j will have pure rotational spectra.

14.17. **(a)** allowed **(b)** forbidden **(c)** forbidden **(d)** forbidden **(e)** forbidden **(f)** allowed **(g)** forbidden **(h)** allowed

14.19. $r = 3.28$ Å

14.20. $r = 1.60$ Å

14.21. 450.5, 900.9, 1351.2, and 1801.6 GHz

14.22. **(a)** $J_{max} \approx 4$ **(b)** $J_{max} \approx 7$

14.23. $T \approx 1600$ K

14.29. $D \approx 4.82 \times 10^{-2}$ cm^{-1}

14.30. Total degrees of freedom, vibrational degrees of freedom: **(a)** 6, 1 **(b)** 9, 3 **(c)** 180, 174 **(d)** 69, 63 **(e)** 54, 48

14.32. CH_3D should have more IR-active vibrations due to loss of symmetry.

14.35. $\tilde{\nu}$(est) $= 1215$ cm^{-1} (not a good approximation!)

14.36. 1661.6 cm^{-1}

14.43. $D_e(\text{HF}) = 47{,}550$ cm^{-1}, $a(\text{HF}) = 2.26 \times 10^{10}$ m^{-1} $= 2.26$ Å^{-1}

14.45. $x_e(\text{HBr}) = 0.02097$, $x_e\nu_e = 55.57$ cm^{-1}

14.50. **(a)** same number of vibrations **(b)** C_2H_2 should have a less number of unique vibrations **(c)** CH_4 should have fewer unique vibrations. **(d)** PF_5 should have fewer unique vibrations.

14.51. **(a)** proper: E, C_3's; improper: σ_v's. **(b)** proper: E, C_3's, C_2's; improper: S_4's, σ_d's.

14.53. **(a)** 6 **(c)** 3 **(d)** 6

14.54. **(a)** 2 **(b)** 6 **(c)** 8 **(d)** 6 **(e)** 2

14.55. The different symmetries will give a different number of IR-measurable vibrations: tetrahedral symmetry gives 2 IR-active vibrations; square planar symmetry (i.e., D_{4h}) yields 3 IR-active vibrations.

14.58. $618\ \text{cm}^{-1} = \nu_2 - \nu_1$, $2337\ \text{cm}^{-1} = \nu_3 - \nu_2 + 2\nu_1$, and $3715\ \text{cm}^{-1} = 2\nu_1 + \nu_3$ or $\nu_2 + \nu_3$.

14.63. $r = 1.00$ Å

14.66. There is no such thing as a $P(0)$ line. P branches are $\Delta J = -1$, and a molecule cannot go from $J = 0$ to $J = -1$.

Chapter 15

15.1. Possible excited states can only have E_{1u} symmetry.

15.3. $R(\text{D}) = 109{,}660\ \text{cm}^{-1}$, $R(\text{T}) = 109{,}670\ \text{cm}^{-1}$

15.4. $15{,}231\ \text{cm}^{-1}$, $20{,}561\ \text{cm}^{-1}$, $23{,}029\ \text{cm}^{-1}$, $24{,}369\ \text{cm}^{-1}$

15.6. $\Delta E = 0$

15.7. **(a)** $L = 2, 1, 0$; $M_L = -2, -1, 0, 1, 2$ (depending on the value of L); $S = 1, 0$; $M_S = -1, 0, 1$ (depending on the value of S); $J = 3, 2, 1, 0$ (depending on the values of L and S); $M_J = -3, -2, -1, 0, 1, 2, 3$ (depending on the value of J).

15.8. $M_S = -\frac{1}{2}$ or $+\frac{1}{2}$ for the H nucleus. If the nucleus and electron angular momenta are coupled, M_S can equal -1, 0, or 1 for the complete atom.

15.9. Aluminum has a single p electron in its highest-filled subshell.

15.10. **(a)** $\ell = 2$, $m_\ell = -2, -1, 0, 1, 2$, $j = \frac{5}{2}$ ($m_j = -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$, or $\frac{5}{2}$) or $j = \frac{3}{2}$ ($m_j = -\frac{3}{2}, -\frac{1}{2}$, or $\frac{1}{2}$)

15.11. $\Delta E = 4 \times 10^{-22}$ J

15.12. **(a)** $^2S_{1/2}$ **(b)** $^2P_{1/2}$ **(c)** $^2D_{3/2}$

15.14. $^3P_0$ is the term symbol of the ground electronic state of C atoms, and is understood to have an energy of 0 with respect to itself.

15.17. $^3F_2$, $^3F_3$, $^3D_1$, $^3D_2$, $^3D_3$, and $^3G_3$

15.20. Heteronuclear diatomic molecules—and their wavefunctions—do not have a center of inversion symmetry element, which is required to use gerade and ungerade labels.

15.21. $^3\Sigma_g^+$, $^3\Sigma_g^-$, $^1\Delta_g$

15.29. There will be no change in the Hückel approximation of ethylene because the hydrogen atom (any isotope) does not contribute to the π orbitals.

15.30. For cyclobutadiene: $\begin{vmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{vmatrix} = 0$

15.31. Cyclopentadiene can accept an electron and have the maximum possible decrease in energy due to delocalization. That is, with 6 π electrons, Cp^- is aromatic.

15.34. **(a)** $C_{4n+2}H_{4n+2}$, $n = 0, 1, 2, \ldots$ can be aromatic. **(b)** $C_{4n+1}H_{4n+1}^-$, $n = 1, 2, \ldots$ can be aromatic. **(c)** $C_{4n}H_{4n}^{-2}$, $n = 1, 2, \ldots$ can be aromatic.

15.35. Heating a laser-active material populates energy levels only thermally, eventually establishing an excited-state population dictated by the Boltzmann distribution. Population inversions won't be achieved.

15.39. ~1.60×10^{25} photons per second

15.41. 1.20×10^8 W

15.42. Because the ratio of spontaneous emission to stimulated emission increases proportional to ν^3 (see equation 15.33), as the frequency increases, spontaneous emission dominates over stimulated emission. This makes it progressively more difficult to construct a laser for shorter and shorter wavelengths of light.

Chapter 16

16.2. 0.06 gauss

16.3. **(a)** Magnetic dipole would be the same. **(b)** See Example 16.2b.

16.7. **(a)** $\Delta E = -2.18 \times 10^{-23}$ J, 0 J, and $+2.18 \times 10^{-18}$ J

16.8. 0.357 T

16.9. $\Delta E\ (M_J = +\frac{3}{2} \rightarrow M_J = -\frac{3}{2}) = 2.23 \times 10^{-27}$ J ($\approx 1.12 \times 10^{-4}\ \text{cm}^{-1}$)

16.11. $g = 1.50115$ vs. 1.5

16.12. $\Delta E = -3.10 \times 10^{-24}$ J, -1.03×10^{-24} J, $+1.03 \times 10^{-24}$ J, and $+\ 3.10 \times 10^{-24}$ J

16.15. 5

16.18. 0.388 T

16.19. $\tilde{\nu} = 0.325\ \text{cm}^{-1}$

16.22. 7 hyperfine absorptions at 3716, 3638, 3560, 3482, 3404, 3326, and 3248 gauss

16.23. The resonant transitions should occur at the same wavelength.

16.24. a, d, f, and g have nonzero nuclear spins and so will show NMR spectra under the right resonant conditions.

16.25. **(a)** 50.5 T **(b)** 8.34 T **(c)** 19.1 T

16.28. $\Delta E = +1.432 \times 10^{-26}$ J, $+4.774 \times 10^{-27}$ J, -4.774×10^{-27} J, and -1.432×10^{-26} J

16.29. $\Delta E = +14.41$ MHz

16.30. Boron NMR are more complex for two reasons: **(a)** There are two common isotopes of B, ^{10}B (~20%) and ^{11}B (~80%); and **(b)** they have different nuclear spins (3 and $\frac{3}{2}$, respectively) and different magnetogyric ratios.

16.31. 154 T

Chapter 17

17.1. One per box: 4 ways. Any number per box: 24 ways.

17.2. 24 ways

17.3. ln (1,000,000!) $\approx 1.281 \times 10^7$. Therefore, 1,000,000! = $e^{1{,}281 \times 10^7}$

17.5. ln (5000!) $\approx$ 37,591, which is the same value as given in the text (*not* from Stirling's approximation)

17.7. On average, there are 25 insects per month over the course of a year.

17.8. **(a)** 113,400 **(b)** 6 **(c)** 20

17.11. Most probable distribution: 1 ball in each of three boxes ($P = 0.50$)

17.15. $N_1/N_0 = 0.38$

17.17. 13.2 K for 1 : 2 $E_1 : E_0$, 38.9 K for 1 : 1 $E_2 : E_0$, 122.5 K for 1 : 1 $E_3 : E_2$

17.19. G is always higher than A.

17.28. The development of statistical thermodynamic equations is based on the statistical behavior of individual particles. Thus, the masses of those individual particles (i.e., atoms or molecules) must be used, not the molar mass.

17.31. $\Lambda(25\text{ K}) = 1.745 \times 10^{-10}$ m, $\Lambda(500\text{ K}) = 3.903 \times 10^{-11}$ m

17.32. At 120 K, krypton is very close to its liquefaction temperature and is not acting like a real gas.

17.33. **(a)** 164.9 J/(mol·K) **(b)** 210.2 J/(mol·K) **(c)** 174.9 J/(mol·K)

17.34. 620 J

17.36. 94,100 K

Chapter 18

18.1. **(a)** 1 **(b)** 1 **(c)** 2

18.4. $q_{elect} = 8.96$ (not much change from 7.82 at 298 K)

18.5. Minimum $q_{elect} = 1$

18.6. q_{elect} (Ni, 298 K) = 5.971 vs. q_{elect} (Ni, 1000 K) = 5.991; q_{elect} (Ni, 5.0 K) = 4.688 vs. q_{elect} (Ni, 298 K) = 5.971

18.7. $q_{elect} \approx 5.89 \times 10^{75}$

18.8. $q_{elect} \approx 10^{128}$

18.9. **(a)** $q_{elect} \approx 13.1$ **(b)** Room temperature has enough thermal energy ($\approx RT$) to break the He_2 "bond," so it probably won't exist at 300 K.

18.11. $q_{H_2}/q_{D_2} = 1/\sqrt{2}$

18.12. q_{vib} (250 K) $\approx 1.3 \times 10^{-18}$; q_{vib} (500 K) $\approx 1.3 \times 10^{-9}$

18.13. $q_{vib} = 1.8 \times 10^{-20}$

18.14. 216 (2), 313 (3), 459, and 779 (3) cm^{-1} (degeneracies in parentheses)

18.15. Minimum $q_{nuc} = 1$, minimum $q_{rot} = 1$ (from equation 18.26)

18.16. $T = 374$ K

18.17. $q_{H_2}/q_{D_2} = 1/2$

18.18. Even-numbered J states are associated with antisymmetric nuclear wavefunctions; odd-numbered J states are associated with symmetric nuclear wavefunctions.

18.20. θ_r should increase because centrifugal distortions will increase the moment of inertia I of the molecule.

18.21. q_{rot} (NH_3) = 74.8

18.25. For HCl, 298 K: $E = -407.8$ kJ/mol, $H = -397.9$ kJ/mol, $G = -456.0$ kJ/mol, $S = 186.5$ J/mol·K

18.34. **(a)** 35.8 N/m or 3.58 mdyn/Å **(b)** 150 cm^{-1}

Chapter 19

19.2. 6.66×10^{-21} J; 4.01 kJ/mol

19.4. **(a)** 1305 m/s **(b)** 285 m/s

19.6. $p \approx 3.68 \times 10^{-21}$ atm $v_{avg} = 184$ m/s

19.7. 213 K, 853 K, 1920 K, 3410 K, 5330 K

19.8. 3×10^{12} K

19.13. ratio = $\sqrt{\frac{3}{2}}$

19.14. **(a)** Using $v \approx 15$ m/s and $dv = 10$ m/s, $G(v) \approx 8.24 \times 10^{-5}$. **(b)** Using $v \approx 1005$ m/s and $dv = 10$ m/s, $G(v) \approx 5.69 \times 10^{-4}$. **(c)** Using $v \approx 10005$ m/s and $dv = 10$ m/s, $G(v) \approx 0$.

19.15. $T \approx 5 \times 10^{-7}$ K

19.20. $\lambda \approx 2.6 \times 10^{12}$ m

19.22. $\lambda \approx 7.65 \times 10^{-10}$ m

19.23. For a given gas, density and temperature are the only variables needed to determine an average collision frequency.

19.24. $z = 2110\ s^{-1}$

19.31. 2.02×10^{14} per second

19.32. $p \approx 664$ bar or 4.98 torr

19.33. 2.85×10^{-6} g of Ar per second

19.36. **(a)** 0.844 cm^2/s

Chapter 20

20.2. rate = 4.06×10^{-7} mol/s

20.3. All rates are 406×10^{-7} mol/s

20.4. rate = $(1.12 \times 10^{-4}\ \text{M}^{-2}\cdot\text{s}^{-1})[\text{A}]^2[\text{B}]^1[\text{C}]^0$

20.7. rate = $(3.34 \times 10^{-2}\ \text{M}^{-1}\cdot\text{s}^{-1})[\text{A}]^1[\text{B}]^1$

20.8. $[\text{A}] = 1.33 \times 10^{-2}$ M

20.9. $\text{M}^{-3}\cdot\text{s}^{-1}$

20.12. 35.2 s

20.13. **(a)** 32.4 s **(b)** 356 s

20.14. **(a)** 32.7 s **(b)** 397 s

20.17. $\dfrac{-d[\text{A}]}{dt} = k[\text{A}]^3$; $\dfrac{1}{2[\text{A}]_t^2} - \dfrac{1}{2[\text{A}]_0^2} = kt$; plot $\dfrac{1}{2[\text{A}]_t^2}$ vs. t, slope = k and intercept = $\dfrac{1}{2[\text{A}]_0^2}$.

20.18. **(a)** $t_{1/2} = \dfrac{3}{2k[\text{A}]_0^2}$ **(b)** $t_{1/2} = \dfrac{3[\text{A}]_0^2}{8k}$

20.19. slope = $-k$; intercept = $[\text{A}]_0$

20.21. $t = \dfrac{[\text{A}]_0}{k}$

20.26. slope = $k/2.303$

20.28. $K \approx 2.9 \times 10^1$

20.31. Initial ratio of (A − B)/(B − C) = 8.98. Equilibrium ratio cannot be determined without knowing the rates of the reverse reactions.

20.33. slope = $-(k_1 + k_2)$

20.43. $E_A \approx 51.9$ kJ

20.44. $A \approx 1.2 \times 10^{55}\ \text{s}^{-1}$

20.45. $A \approx 1.21 \times 10^{-11}\ \text{s}^{-1}$

20.46. **(a)** order = 2 **(b)** k (100°C) = $2.08 \times 10^{-6}\ \text{M}^{-1}\cdot\text{s}^{-1}$

20.49. **(a)** E_A = 159 kJ/mol **(b)** $A = 1.8 \times 10^{38}\ \text{s}^{-1}$

20.60. $V \approx 2.6 \times 10^{-6}$ mol/s

20.63. I_2 should proceed most easily.

Chapter 21

21.6. **(a)** 3 unit cells **(b)** 2 unit cells **(c)** 6 unit cells **(d)** 1 unit cell (See Table 21.1 for the crystal systems that fit the given requirements.)

21.9. $r_{\text{max}} = (\sqrt{3}/4)a$

21.12. 4 formula units; face-centered cubic

21.13. FeS_2

21.14. $d = 2.784\ \text{g/cm}^3$

21.21. θ = 8.2° and 16.5°

21.22. θ = 12.3° (or 25.2° or 39.7° or 58.5°)

21.23. $N_A \approx 6.0320 \times 10^{23}$

21.30. **(a)** 15.5° **(b)** 22.3°

21.31. fcc, a = 4.933 Å

21.32. KBr diffracts the given X rays at θ = 11.7°, 13.5°, 19.3°, 22.8°, 23.9°, and 27.9°.

21.35. The sample *could* be MgO, since the ions in this compound are isoelectronic and would have similar scattering factors.

21.36. **(a)** fcc, NaCl-type **(b)** sc **(c)** sc

21.37. **(a)** rutile **(b)** fluorite **(c)** rutile

21.40. coordination number = 8

21.41. coordination number (Ca, fluorite) = 8, coordination number (F, fluorite) = 4; coordination number (Ti, rutile) = 6, coordination number (O, rutile) = 3.

21.43. **(a)** K^+ (g) $+\text{F}^-$ (g) → KF (crystal)

21.46. **(a)** 399 kJ/mol (coulombic) vs. 636 kJ/mol (lattice energy)

21.47. ρ = 0.307 Å

Chapter 22

22.2. 4.355×10^5 dyn/cm

22.3. **(a)** 1.36×10^{-4} J

22.6. **(a)** $\Delta T \approx 10.8$°C

22.7. $\gamma < {\sim}4 \times 10^{-2}\ \text{erg/cm}^2$

22.15. **(a)** 9600 $\text{dyn/cm}^2 \approx 0.72$ torr

22.18. **(b)** $p_{\text{vapor}} \approx 25.06$ mmHg

22.20. 49.9°

22.24. **(a)** 3.988 Å

22.30. 3.54×10^8 molecules of gas per cubic centimeter

22.31. ~0.01 s

22.32. 7.5×10^8 L

22.33. **(a)** heterogeneous **(b)** heterogeneous **(c)** homogeneous

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The Periodic Table

92	Atomic number
U	Symbol
Uranium 238.0289	Atomic weight

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A	
1 **H** Hydrogen 1.0079																	2 **He** Helium 4.0026	1
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.0122											5 **B** Boron 10.811	6 **C** Carbon 12.011	7 **N** Nitrogen 14.0067	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984	10 **Ne** Neon 20.1797	2
11 **Na** Sodium 22.9898	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.9815	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.9738	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948	3
19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.9559	22 **Ti** Titanium 47.88	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.9380	26 **Fe** Iron 55.847	27 **Co** Cobalt 58.9332	28 **Ni** Nickel 58.693	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.9216	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80	4
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*Elements 110–112 have not yet been named.

Physical Constants

Quantity	Symbol	Value	Unit
Speed of light in vacuum	c	2.99792458×10^{8}	m/s
Permittivity of free space	ε_0	$8.854187817 \times 10^{-12}$	C^2/J·m
Gravitation constant	G	6.673×10^{-11}	N·m^2/kg^2
Planck's constant	h	$6.62606876 \times 10^{-34}$	J·s
Elementary charge	e	$1.602176462 \times 10^{-19}$	C
Electron mass	m_e	$9.10938188 \times 10^{-31}$	kg
Proton mass	m_p	$1.67262158 \times 10^{-27}$	kg
Bohr radius	a_0	$5.291772083 \times 10^{-11}$	m
Rydberg constant	R	109737.31568	cm^{-1}
Avogadro's constant	N_A	$6.02214199 \times 10^{23}$	mol^{-1}
Faraday's constant	$\mathcal{F}$	96485.3415	C/mol
Ideal gas constant	R	8.314472	J/mol·K
		0.0820568	L·atm/mol·K
		0.08314472	L·bar/mol·K
		1.98719	cal/mol·K
Boltzmann's constant	k, k_B	$1.3806503 \times 10^{-23}$	J/K
Stefan-Boltzmann constant	σ	5.670400×10^{-8}	W/m^2·K^4
Bohr magneton	μ_B	$9.27400899 \times 10^{-24}$	J/T
Nuclear magneton	μ_N	$5.05078317 \times 10^{-27}$	J/T

Source: Excerpted from Peter J. Mohr and Barry N. Taylor, CODATA Recommended Values of the Fundamental Physical Constants, *J. Phys. Chem. Ref. Data*, vol. 28, 1999.