account for the fact that platinum will dissolve in a mixture of hydrochloric acid and nitric acid (*aqua regia*) but will not dissolve in either acid alone.

77. (a) One method to reduce the concentration of unwanted $Fe^{3+}(aq)$ in a solution of $Fe^{2+}(aq)$ is to drop a piece of metallic iron into the storage container. Write the reaction that removes the Fe^{3+}, and compute its standard cell potential.
    (b) By referring to problem 23, suggest a way to remove unwanted $Mn^{3+}(aq)$ from solutions of $Mn^{2+}(aq)$.

78. (a) Based only on the standard reduction potentials for the $Cu^{2+}|Cu^{+}$ and the $I_2(s)|I^-$ half-reactions, would you expect $Cu^{2+}(aq)$ to be reduced to $Cu^{+}(aq)$ by $I^-(aq)$?
    (b) The formation of solid CuI plays a role in the interaction between $Cu^{2+}(aq)$ and $I^-(aq)$.

$$Cu^{2+}(aq) + I^-(aq) + e^- \rightleftharpoons CuI(s) \qquad \mathcal{E}^\circ = 0.86\ \text{V}$$

Taking into account this added information, do you expect Cu^{2+} to be reduced by iodide ion?

79. In some old European churches, the stained-glass windows have so darkened from corrosion and age that hardly any light comes through. Microprobe analysis showed that tiny cracks and defects on the glass surface were enriched in insoluble Mn(III) and Mn(IV) compounds. From Appendix E, suggest a reducing agent and conditions that might successfully convert these compounds to soluble Mn(II) without simultaneously reducing Fe(III) (which gives the glass its colors) to Fe(II). Take MnO_2 as representative of the insoluble Mn(III) and Mn(IV) compounds.

80. (a) Calculate the half-cell potential for the reaction

$$O_2(g) + 4\ H_3O^+(aq) + 4\ e^- \longrightarrow 6\ H_2O(\ell)$$

at pH 7 with the oxygen pressure at 1 atm.
    (b) Explain why aeration of solutions of I^- leads to their decomposition. Write a balanced equation for the redox reaction that occurs.
    (c) Will the same problem arise with solutions containing Br^- or Cl^-? Explain.
    (d) Will decomposition be favored or opposed by increasing acidity?

81. An engineer needs to prepare a galvanic cell that uses the reaction

$$2\ Ag^+(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + 2\ Ag(s)$$

and generates an initial voltage of 1.50 V. She has 0.010 M $AgNO_3(aq)$ and 0.100 M $Zn(NO_3)_2(aq)$ solutions, as well as electrodes of metallic copper and silver, wires, containers, water, and a KNO_3 salt bridge. Sketch the cell. Clearly indicate the concentrations of all solutions.

82. Consider a galvanic cell for which the anode reaction is

$$Pb(s) \longrightarrow Pb^{2+}(1.0 \times 10^{-2}\ \text{M}) + 2\ e^-$$

and the cathode reaction is

$$VO^{2+}(0.10\ \text{M}) + 2\ H_3O^+(0.10\ \text{M}) + e^- \longrightarrow V^{3+}(1.0 \times 10^{-5}\ \text{M}) + 3\ H_2O(\ell)$$

The measured cell voltage is 0.640 V.
    (a) Calculate $\mathcal{E}^\circ$ for the $VO^{2+}|V^{3+}$ half-reaction, using $\mathcal{E}^\circ(Pb^{2+}|Pb)$ from Appendix E.
    (b) Calculate the equilibrium constant (K) at 25°C for the reaction

$$Pb(s) + 2\ VO^{2+}(aq) + 4\ H_3O^+(aq) \rightleftharpoons Pb^{2+}(aq) + 2\ V^{3+}(aq) + 6\ H_2O(\ell)$$

83. Suppose we construct a pressure cell in which the gas pressures differ in the two half-cells. Suppose such a cell consists of a $Cl_2(0.010\ \text{atm})|Cl^-(1\ \text{M})$ half-cell connected to a $Cl_2(0.50\ \text{atm})|Cl^-(1\ \text{M})$ half-cell. Determine which half-cell will be the anode, write the overall equation for the reaction, and calculate the cell voltage.

84. A student decides to measure the solubility of lead sulfate in water and sets up the electrochemical cell

$$Pb|PbSO_4|SO_4^{2-}(aq,\ 0.0500\ \text{M})||Cl^-(aq,\ 1.00\ \text{M})|AgCl|Ag$$

At 25°C the student finds the cell voltage to be 0.546 V, and from Appendix E the student finds

$$AgCl(s) + e \rightleftharpoons Ag(s) + Cl^-(aq) \qquad \mathcal{E}^\circ = 0.222\ \text{V}$$

What does he find for the K_{sp} of $PbSO_4$?

85. A wire is fastened across the terminals of the Leclanché cell in Figure 17.6. Indicate the direction of electron flow in the wire.

86. Overcharging a lead–acid storage battery can generate hydrogen. Write a balanced equation to represent the reaction taking place.

87. An ambitious chemist discovers an alloy electrode that is capable of catalytically converting ethanol reversibly to carbon dioxide at 25°C according to the half-reaction

$$C_2H_5OH(\ell) + 15\ H_2O(\ell) \longrightarrow 2\ CO_2(g) + 12\ H_3O^+(aq) + 12\ e^-$$

Believing that this discovery is financially important, the chemist patents its composition and designs a fuel cell that may be represented as

$$Alloy|C_2H_5OH(\ell)|CO_2(g) + H_3O^+(1\ \text{M})||H_3O^+(1\ \text{M})|O_2|Ni$$

    (a) Write the half-reaction occurring at the cathode.
    (b) Using data from Appendix D, calculate $\Delta\mathcal{E}^\circ$ for the cell at 25°C.
    (c) What is the $\mathcal{E}^\circ$ value for the ethanol half-cell?

88. Iron or steel is often covered by a thin layer of a second metal to prevent rusting: Tin cans consist of steel covered with tin, and galvanized iron is made by coating iron with a layer of zinc. If the protective layer is broken, however, iron will rust more readily in a tin can than in galvanized iron. Explain this observation by comparing the half-cell potentials of iron, tin, and zinc.

89. An electrolysis cell contains a solution of 0.10 M $NiSO_4$. The anode and cathode are both strips of Pt foil. Another electrolysis cell contains the same solution, but the electrodes are strips of Ni foil. In each case a current of 0.10 A flows through the cell for 10 hours.
    (a) Write a balanced equation for the chemical reaction that occurs at the anode in each cell.
    (b) Calculate the mass, in grams, of the product formed at the anode in each cell. (The product may be a gas, a solid, or an ionic species in solution.)

90. A potential difference of 2.0 V is impressed across a pair of inert electrodes (e.g., platinum) that are immersed in a 0.050 M aqueous KBr solution. What are the products that form at the anode and the cathode?

91. An aqueous solution is simultaneously 0.10 M in $SnCl_2$ and in $CoCl_2$.

(a) If the solution is electrolyzed, which metal will appear first?

(b) At what decomposition potential will that metal first appear?

(c) As the electrolysis proceeds, the concentration of the metal being reduced will drop and the voltage will change. How complete a separation of the metals using electrolysis is theoretically possible? In other words, at the point where the second metal begins to form, what fraction of the first metal is left in solution?

92. A 55.5-kg slab of crude copper from a smelter has a copper content of 98.3%. Estimate the time required to purify it electrochemically if it is used as the anode in a cell that has acidic copper(II) sulfate as its electrolyte and a current of 2.00×10^3 A is passed through the cell.

93. Sheet iron can be galvanized by passing a direct current through a cell containing a solution of zinc sulfate between a graphite anode and the iron sheet. Zinc plates out on the iron. The process can be made continuous if the iron sheet is a coil that unwinds as it passes through the electrolysis cell and coils up again after it emerges from a rinse bath. Calculate the cost of the electricity required to deposit a 0.250-mm-thick layer of zinc on both sides of an iron sheet that is 1.00 m wide and 100 m long, if a current of 25 A at a voltage of 3.5 V is used and the energy efficiency of the process is 90%. The cost of electricity is 10 cents per kilowatt–hour (1 kWh = 3.6 MJ). Consult Appendix F for data on zinc.

CUMULATIVE PROBLEMS

94. A 1.0 M solution of NaOH is electrolyzed, generating $O_2(g)$ at the anode. A current of 0.15 A is passed through the cell for 75 minutes. Calculate the volume of (wet) oxygen generated in this period if the temperature is held at 25°C and the total pressure is 0.985 atm. (*Hint:* Use the vapor pressure of water at this temperature from Table 10.1.)

95. Use standard entropies from Appendix D to predict whether the standard voltage of the $\mathrm{Cu}|\mathrm{Cu}^{2+}||\mathrm{Ag}^{+}|\mathrm{Ag}$ cell (diagrammed in Figure 17.2) will increase or decrease if the temperature is raised above 25°C.

96. About 50,000 kJ of electrical energy is required to produce 1.0 kg of Al from its $Al(OH)_3$ ore. The major energy cost in recycling aluminum cans is the melting of the aluminum. The enthalpy of fusion of Al(*s*) is 10.7 kJ mol^{-1}. Compare the energy cost for making new aluminum with that for recycling.

97. (a) Use the following half-reactions and their reduction potentials to calculate the K_{sp} of AgBr:

$$\mathrm{Ag}^+(aq) + e^- \longrightarrow \mathrm{Ag}(s) \qquad \mathscr{E}° = 0.7996\ \mathrm{V}$$

$$\mathrm{AgBr}(s) + e^- \longrightarrow \mathrm{Ag}(s) + \mathrm{Br}^-(aq) \qquad \mathscr{E}° = 0.0713\ \mathrm{V}$$

(b) Estimate the solubility of AgBr in 0.10 M NaBr(*aq*).

98. Amounts of iodine dissolved in aqueous solution, $I_2(aq)$, can be determined by titration with thiosulfate ion ($S_2O_3^{2-}$). The thiosulfate ion is oxidized to $S_4O_6^{2-}$ while the iodine is reduced to iodide ion. Starch is used as an indicator because it has a strong blue color in the presence of dissolved iodine.

(a) Write a balanced equation for this reaction.

(b) If 56.40 mL of 0.100 M $S_2O_3^-$ solution is used to reach the endpoint of a titration of an unknown amount of iodine, calculate the number of moles of iodine originally present.

(c) Combine the appropriate half-cell potentials from Appendix E with thermodynamic data from Appendix D for the equilibrium

$$I_2(s) \rightleftharpoons I_2(aq)$$

to calculate the equilibrium constant at 25°C for the reaction in part (a).

UNIT V

Rates of Chemical and Physical Processes


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Zinc reacts readily with aqueous hydrochloric acid to give hydrogen gas and aqueous zinc chloride.

Thermodynamics explains *why* chemical reactions occur; minimizing the Gibbs free energy is the driving force toward chemical equilibrium. Thermodynamics provides deep insight into the nature of chemical equilibrium, but it gives no answer to the crucial question of how rapidly that equilibrium is achieved.

Chemical kinetics explains *how* reactions occur by studying their rates and mechanisms. Chemical kinetics explains how the speeds of different chemical reactions vary from explosive rapidity to glacial sluggishness and how slow reactions can be accelerated by materials called catalysts. Chemical kinetics has enormous practical importance because it provides the basis for optimizing conditions to carry out chemical reactions at reasonable speed, under proper control.

The central goal in chemical kinetics is to find the relationship between the rate of a reaction and the amount of reactants present. Once this connection is established, the influence of external conditions—principally the temperature—can be explored.

Nuclear chemistry represents a particularly simple limiting form of kinetics in which unstable nuclei decay with a constant probability during any time interval. Its richness arises from the multiplicity of decay paths that are possible, which arise from the mass-energy relationships that determine nuclear stability.

Molecules absorb and emit light at specific wavelengths determined by the separations between molecular energy levels. Through quantum mechanics, molecular spectroscopy connects these specific wavelengths to models of molecular structure, and so determines the structure of molecules from their interaction with light. Light can induce chemical reactions through pathways not available by thermal excitation. Both spectroscopy and photochemistry rely on tools of chemical kinetics to describe rates of light-induced processes.

UNIT CHAPTERS

CHAPTER 18
Chemical Kinetics

CHAPTER 19
Nuclear Chemistry

CHAPTER 20
Interaction of Molecules with Light

UNIT GOALS

- To relate the rate of a chemical reaction to the instantaneous concentration(s) of reactants by developing the rate law and the rate constant for the reaction
- To describe the influence of temperature on the reaction rate by identifying the activation energy for the reaction
- To explain the mechanism of a complex reaction by identifying the separate elementary reaction steps through which it proceeds
- To explain the role of catalysts in manipulating reaction rates
- To develop an elementary description of the rates of nuclear reactions, emphasizing the half-life of radioactive species
- To survey the applications and consequences of nuclear reactions in medicine, biology, energy production, and the environment
- To develop methods of molecular spectroscopy for structure determination
- To relate the initiation of photochemical reactions to the wavelength of light, and survey consequences of photochemical reactions in the atmosphere

CHAPTER 18

Chemical Kinetics

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Powdered chalk (mostly calcium carbonate $CaCO_3$) reacts rapidly with dilute hydrochloric acid because it has a large total surface area. A stick of chalk has a much smaller surface area, so it reacts much more slowly.

Why do some chemical reactions proceed with lightning speed when others require days, months, or even years to produce detectable amounts of products? How do catalysts increase the rates of chemical reactions? Why do small changes in temperature often have such large effects on the cooking rate of food? How does a study of the rate of a chemical reaction inform us about the way in which molecules combine to form products? All of these questions involve studies of reaction rates, which is the subject of chemical kinetics.

Chemical kinetics is a complex subject, and at present it is not understood nearly as well as chemical thermodynamics. For many reactions the equilibrium constants are known accurately, but the rates and detailed reaction pathways remain poorly understood. This is particularly true of reactions in which many species participate in the overall process connecting reactants to products. One good example is the reaction

$$5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H_3O^+(aq) \longrightarrow 5\ Fe^{3+}(aq) + Mn^{2+}(aq) + 12\ H_2O(\ell)$$

We can measure the equilibrium constant for this reaction easily from the voltage of a galvanic cell, and then calculate from it the equilibrium concentrations that will result from arbitrary initial conditions. It is considerably harder to determine the exact pathway by which the reaction goes from reactants to products. This path certainly does *not* involve the simultaneous collision of five Fe^{2+} ions and one MnO_4^- ion with eight H_3O^+ ions, because such a collision would be exceedingly rare. Instead, the path proceeds through a series of elementary steps involving two or at most three ions, such as

$$Fe^{2+}(aq) + MnO_4^-(aq) \longrightarrow Fe^{3+}(aq) + MnO_4^{2-}(aq)$$

$$MnO_4^{2-}(aq) + H_3O^+(aq) \longrightarrow HMnO_4^-(aq) + H_2O(\ell)$$

$$HMnO_4^-(aq) + Fe^{2+}(aq) \longrightarrow HMnO_4^{2-}(aq) + Fe^{3+}(aq)$$

Other postulated steps take the process to its final products. Some of these steps are slow, and others fast; taken together they constitute the **reaction mechanism.**

The primary goal of chemical kinetics is to deduce the mechanism of a reaction from experimental studies of its rate. For this, we have to measure how the rate depends on the concentrations of the reacting species. This chapter lays out the methods and concepts for measuring and interpreting reaction rates and for identifying the mechanism.

18.1 Rates of Chemical Reactions

The speed of a reaction depends on many factors. Concentrations of reacting species certainly play a major role in speeding up or slowing down a particular reaction (Fig. 18.1). As we will see in Section 18.5, many reaction rates are extremely sensitive to temperature. This means that careful control of temperature is critical

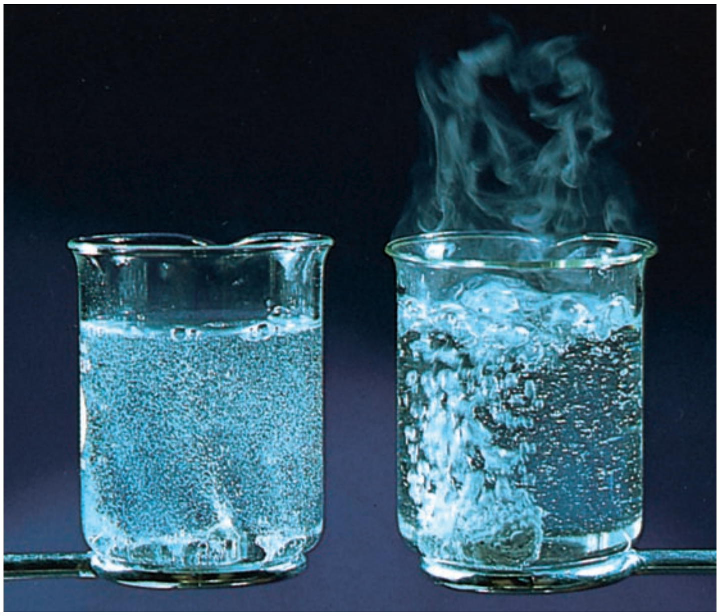

FIGURE 18.1 The rate of reaction of zinc with aqueous sulfuric acid depends on the concentration of the acid. The dilute solution reacts slowly (left), and the more concentrated solution reacts rapidly (right).

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for quantitative measurements in chemical kinetics. Finally, the rate often depends crucially on the physical forms of the reactants. An iron nail oxidizes only very slowly in dry air to iron oxide, but steel wool burns spectacularly in oxygen (Fig. 18.2). Because the quantitative study of heterogeneous reactions—those involving two or more phases, such as a solid and a gas—is difficult, we begin with homogeneous reactions, which take place entirely within the gas phase or solution. In Section 18.7 we turn briefly to some important aspects of heterogeneous reactions.


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FIGURE 18.2 Steel wool burning in oxygen.

Measuring Reaction Rates

A kinetics experiment measures the rate of change of the concentration of a substance participating in a chemical reaction. How can we experimentally monitor a changing concentration? If the reaction is slow enough, we can let it run for a measured time and then abruptly "quench" (effectively stop) it by rapidly cooling the reaction mixture sufficiently. At that low temperature the composition of the reaction mixture remains constant, so we have time to analyze the mixture for some particular reactant or product. This procedure is not useful for rapid reactions, especially those involving gas mixtures, because they are difficult to cool quickly. An alternative is to probe the concentrations by the absorption of light. Chapter 20 shows that different molecules absorb at different wavelengths. If a wavelength is absorbed by only one particular reactant or product, measuring the amount of light absorbed by the reaction mixture at that wavelength determines the concentration of the absorbing species. A series of such measurements at different times reveals the rate of change of the concentration. Often, a flash of light can also be used to initiate a very fast reaction, whose rate is then tracked by measuring absorption at a particular wavelength.

The average rate of a reaction is analogous to the average speed of a car. If the average position of a car is recorded at two different times, then

$$\text{average speed} = \frac{\text{distance traveled}}{\text{time elapsed}} = \frac{\text{change in location}}{\text{change in time}}$$

In the same way, the **average reaction rate** is obtained by dividing the change in concentration of a reactant or product by the time interval over which that change occurs:

$$\text{average reaction rate} = \frac{\text{change in concentration}}{\text{change in time}}$$

If concentration is measured in mol L^{-1} and time in seconds, then the rate of a reaction has units of mol L^{-1} s^{-1}.

Consider a specific example. In the gas-phase reaction

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

NO_2 and CO are consumed as NO and CO_2 are produced. If a probe can measure the NO concentration, the average rate of reaction can be estimated from the ratio of the change in NO concentration $\Delta[NO]$ to the time interval Δt:

$$\text{average rate} = \frac{\Delta[NO]}{\Delta t} = \frac{[NO]_f - [NO]_i}{t_f - t_i}$$

This estimate depends on the time interval Δt that is selected, because the rate at which NO is produced changes with time. From the data in Figure 18.3, the average rate of reaction during the first 50 s is

$$\text{average rate} = \frac{\Delta[NO]}{\Delta t} = \frac{(0.0160 - 0) \text{ mol L}^{-1}}{(50 - 0) \text{ s}} = 3.2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

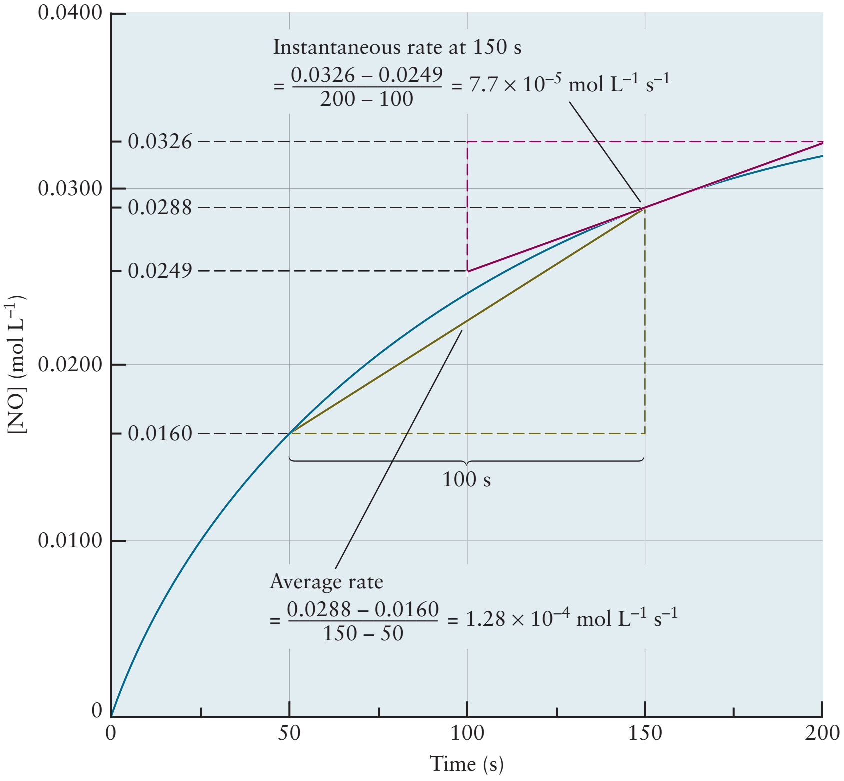


FIGURE 18.3 A graph of the concentration of NO against time in the reaction $NO_2 + CO \longrightarrow NO + CO_2$. The average rate during the time interval from 50 to 150 seconds is obtained by dividing the change in NO concentration by the duration of the interval (green box). Note that the average rate (green line) underestimates the true production rate over the time interval. The instantaneous rate 150 seconds after the start of the reaction is found by calculating the slope of the line tangent to the curve at that point (red box).

During the second 50 s, the average rate is 1.6×10^{-4} mol L^{-1} s^{-1}, and during the third 50 s it is 9.6×10^{-5} mol L^{-1} s^{-1}. Clearly, this reaction slows as it progresses, and its average rate indeed depends on the time interval chosen. Figure 18.3 shows a graphical method for determining average rates. The average rate is the slope of the straight line connecting the concentrations at the initial and final points of a time interval.

The **instantaneous rate** of a reaction is obtained by considering smaller and smaller time increments Δt (with correspondingly smaller values of Δ[NO]). As Δt approaches 0, the rate becomes the slope of the line tangent to the curve at time t (see Fig. 18.3). This slope is written as the derivative of [NO] with respect to time:

$$\text{instantaneous rate} = \text{limit}_{\Delta t \to 0} \frac{[\mathrm{NO}]_{t+\Delta t} - [\mathrm{NO}]_t}{\Delta t} = \frac{d[\mathrm{NO}]}{dt}$$

Throughout the rest of this book, we refer to the instantaneous rate simply as the *rate*. The instantaneous rate of a reaction at the moment that it begins (at $t = 0$) is the **initial rate** of that reaction.

The rate of this sample reaction could just as well have been measured by monitoring changes in the concentration of CO_2, NO_2, or CO instead of NO. Because every molecule of NO produced is accompanied by one molecule of CO_2, the rate of increase of CO_2 concentration is the same as that of NO. The concentrations of the two reactants, NO_2 and CO, *decrease* at the same rate that the concentrations of the products increase, because the coefficients in the balanced equation are also both equal to 1. This is summarized as

$$\text{rate} = -\frac{d[\mathrm{NO_2}]}{dt} = -\frac{d[\mathrm{CO}]}{dt} = \frac{d[\mathrm{NO}]}{dt} = \frac{d[\mathrm{CO_2}]}{dt}$$

Another gas-phase reaction is

$$2\ \mathrm{NO_2}(g) + \mathrm{F_2}(g) \longrightarrow 2\ \mathrm{NO_2F}(g)$$

This equation states that two molecules of NO_2 disappear and two molecules of NO_2F appear for each molecule of F_2 that reacts. Thus, the NO_2 concentration changes twice as fast as the F_2 concentration; the NO_2F concentration also changes twice as fast and has the opposite sign. We write the rate in this case as

$$\text{rate} = -\frac{1}{2}\frac{d[NO_2]}{dt} = -\frac{d[F_2]}{dt} = \frac{1}{2}\frac{d[NO_2F]}{dt}$$

The rate of change of concentration of each species is divided by its coefficient in the balanced chemical equation. Rates of change of reactants appear with negative signs and those of products with positive signs. For the general reaction

$$aA + bB \longrightarrow cC + dD$$

the rate is

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt} \qquad [18.1]$$

These relations hold true provided there are no transient intermediate species or, if there are intermediates, their concentrations are independent of time for most of the reaction period.

18.2 Rate Laws

In discussing chemical equilibrium we stressed that both forward and reverse reactions can occur; once products are formed, they can react back to give the original reactants. The net rate is the difference:

$$\text{net rate} = \text{forward rate} - \text{reverse rate}$$

Strictly speaking, measurements of concentration give the net rate rather than simply the forward rate. Near the beginning of a reaction that starts from pure reactants the concentrations of reactants are far higher than those of products, and the reverse rate can be neglected. In addition, many reactions go to "completion" ($K \gg 1$). This means they have a measurable rate only in the forward direction, or else the experiment can be arranged so that the products are removed as they are formed. This section focuses on forward rates exclusively.

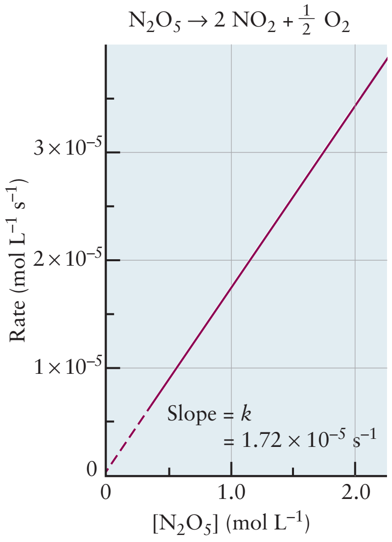


FIGURE 18.4 The rate of decomposition of $N_2O_5(g)$ at 25°C is proportional to its concentration. The slope of this line is equal to the rate constant k for the reaction.

Order of a Reaction

The forward rate of a chemical reaction depends on the concentrations of the reactants. As an example, consider the decomposition of gaseous dinitrogen pentaoxide (N_2O_5). This compound is a white solid that is stable below 0°C but decomposes when vaporized:

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

The rate of the reaction depends on the concentration of $N_2O_5(g)$. Figure 18.4 shows the graph of rate versus concentration to be a straight line that can be extrapolated to pass through the origin. So, the rate can be written

$$\text{rate} = k[N_2O_5]$$

This relation between the rate of a reaction and concentration is called a **empirical rate expression** or **rate law,** and the proportionality constant k is called the **rate constant** for the reaction. Like an equilibrium constant, a rate constant is independent of concentration but depends on temperature, as we describe in Section 18.5.

For many (but not all) reactions with a single reactant, the rate is proportional to the concentration of that reactant raised to a power. That is, the rate expression for

$$aA \longrightarrow \text{products}$$

frequently has the form

$$\text{rate} = k[A]^n$$

It is important to note that the power n in the rate expression has no direct relation to the coefficient a in the balanced chemical equation. This number has to be determined experimentally for each rate law. For the decomposition of ethane at high temperatures and low pressures,

$$C_2H_6(g) \longrightarrow 2\ CH_3(g)$$

the rate expression has the form

$$\text{rate} = k[C_2H_6]^2$$

Therefore, $n = 2$ even though the coefficient in the chemical equation is 1.

The power to which the concentration is raised is called the **order** of the reaction with respect to that reactant. Thus, the decomposition of N_2O_5 is **first order,** whereas that of C_2H_6 is **second order.** Some processes are **zeroth order** over a range of concentrations. Because $[A]^0 = 1$, such reactions have rates that are independent of concentration:

$$\text{rate} = k \qquad \text{(for zeroth-order kinetics)}$$

The order of a reaction does not have to be an integer; fractional powers are sometimes found. At 450 K, the decomposition of acetaldehyde (CH_3CHO) is described by the rate expression

$$\text{rate} = k[CH_3CHO]^{3/2}$$

These examples demonstrate that reaction order is an experimentally determined property that cannot be predicted from the form of the chemical equation.

The following example illustrates how the order of a reaction can be deduced from experimental data.

EXAMPLE 18.1

At elevated temperatures, HI reacts according to the chemical equation

$$2\ HI(g) \longrightarrow H_2(g) + I_2(g)$$

At 443°C, the rate of the reaction increases with concentration of HI as follows:

[HI] (mol L^{-1})	0.0050	0.010	0.020
Rate (mol L^{-1} s^{-1})	7.5×10^{-4}	3.0×10^{-3}	1.2×10^{-2}

(a) Determine the order of the reaction and write the rate expression.

(b) Calculate the rate constant, and give its units.

(c) Calculate the reaction rate for a 0.0020 M concentration of HI.

SOLUTION

(a) The rate expressions at two different concentrations $[HI]_1$ and $[HI]_2$ are

$$\text{rate}_1 = k([HI]_1)^n$$

$$\text{rate}_2 = k([HI]_2)^n$$

After dividing the second equation by the first, the rate constant k drops out, leaving the reaction order n as the only unknown quantity.

$$\frac{\text{rate}_2}{\text{rate}_1} = \left(\frac{[\text{HI}]_2}{[\text{HI}]_1}\right)^n$$

We can now substitute any two sets of data into this equation and solve for n. Taking the first two sets with $[\text{HI}]_1 = 0.0050$ M and $[\text{HI}]_2 = 0.010$ M gives

$$\frac{3.0 \times 10^{-3}}{7.5 \times 10^{-4}} = \left(\frac{0.010}{0.0050}\right)^n$$

which simplifies to

$$4 = (2)^n$$

By inspection, $n = 2$, so the reaction is second order in HI. When the solution of the equation is less obvious, we can take the logarithms of both sides, giving (in this case)

$$\log_{10} 4 = n \log_{10} 2$$

$$n = \frac{\log_{10} 4}{\log_{10} 2} = \frac{0.602}{0.301} = 2$$

The rate expression has the form

$$\text{rate} = k[\text{HI}]^2$$

(b) The rate constant k is calculated by inserting any of the sets of data into the rate expression. Taking the first set gives

$$7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} = k(0.0050 \text{ mol L}^{-1})^2$$

Solving for k gives

$$k = 30 \text{ L mol}^{-1} \text{ s}^{-1}$$

(c) Finally, the rate is calculated for [HI] = 0.0020 M:

$$\begin{aligned}\text{rate} = k[\text{HI}]^2 &= (30 \text{ L mol}^{-1} \text{ s}^{-1})(0.0020 \text{ mol L}^{-1})^2 \\ &= 1.2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}\end{aligned}$$

So far, each example reaction rate has depended only on a single concentration. In reality, many rates depend on the concentrations of two or more different chemical species, and the rate expression is written in a form such as

$$\text{rate} = -\frac{1}{a}\frac{d[\text{A}]}{dt} = k[\text{A}]^m[\text{B}]^n$$

Again the exponents m and n do not derive from the coefficients in the balanced equation for the reaction; they must be determined experimentally and are usually integers or half-integers.

The exponents $m, n, \ldots$ give the order of the reaction, just as in the simpler case where only one concentration appeared in the rate expression. The preceding reaction is said to be mth order in A, meaning that a change in the concentration of A by a certain factor leads to a change in the rate by that factor raised to the mth power. The reaction is nth order in B, and the **overall reaction order** is $m + n$. For the reaction

$$\text{H}_2\text{PO}_2^-(aq) + \text{OH}^-(aq) \longrightarrow \text{HPO}_3^{2-}(aq) + \text{H}_2(g)$$

the experimentally determined rate expression is

$$\text{rate} = k[\text{H}_2\text{PO}_2^-][\text{OH}^-]^2$$

so the reaction is said to be first order in $\text{H}_2\text{PO}_2^-(aq)$ and second order in $\text{OH}^-(aq)$, with an overall reaction order of 3. The units of k depend on the reaction order. If all concentrations are expressed in mol L^{-1} and if $p = m + n + \cdots$ is the overall reaction order, then k has units of $\text{mol}^{-(p-1)}\ \text{L}^{p-1}\ \text{s}^{-1}$.

EXAMPLE 18.2

Use the preceding rate expression to determine the effect of the following changes on the rate of decomposition of $H_2PO_2^-(aq)$:

(a) Tripling the concentration of $H_2PO_2^-(aq)$ at constant pH

(b) Changing the pH from 13 to 14 at a constant concentration of $H_2PO_2^-(aq)$

SOLUTION

(a) Because the reaction is first order in $H_2PO_2^-(aq)$, tripling this concentration will triple the reaction rate.

(b) A change in pH from 13 to 14 corresponds to an increase in the $OH^-(aq)$ concentration by a factor of 10. Because the reaction is second order in $OH^-(aq)$ (that is, this term is squared in the rate expression), this will increase the reaction rate by a factor of 10^2, or 100.

Related Problems: 5, 6

Rate expressions that depend on more than one concentration are more difficult to obtain experimentally than those that depend just on one. One method is to find the instantaneous initial rates of reaction for several values of one of the concentrations, holding the other initial concentrations fixed from one run to the next. The experiment can then be repeated, changing one of the other concentrations. The following example illustrates this procedure.

EXAMPLE 18.3

The reaction of $NO(g)$ with $O_2(g)$ gives $NO_2(g)$:

$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$$

From the dependence of the initial rate $(-\frac{1}{2}\,d[NO]/dt)$ on the initial concentrations of NO and O_2, determine the rate expression and the value of the rate constant.

[NO] (mol L^{-1})	[O_2] (mol L^{-1})	Initial Rate (mol L^{-1} s^{-1})
1.0×10^{-4}	1.0×10^{-4}	2.8×10^{-6}
1.0×10^{-4}	3.0×10^{-4}	8.4×10^{-6}
2.0×10^{-4}	3.0×10^{-4}	3.4×10^{-5}

SOLUTION

When $[O_2]$ is multiplied by 3 (with [NO] constant), the rate is also multiplied by 3 (from 2.8×10^{-6} to 8.4×10^{-6}), so the reaction is first order in O_2. When [NO] is multiplied by 2 (with $[O_2]$ constant), the rate is multiplied by

$$\frac{3.4 \times 10^{-5}}{8.4 \times 10^{-6}} \approx 4 = 2^2$$

so the reaction is second order in NO. Thus, the form of the rate expression is

$$\text{rate} = k[O_2][NO]^2$$

To evaluate k, we insert any set of data into the equation. From the first set,

$$2.8 \times 10^{-6}\ \text{mol L}^{-1}\ \text{s}^{-1} = k(1.0 \times 10^{-4}\ \text{mol L}^{-1})(1.0 \times 10^{-4}\ \text{mol L}^{-1})^2$$

$$k = 2.8 \times 10^{6}\ \text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$$

Related Problems: 7, 8

Integrated Rate Laws

Measuring an initial rate involves determining small changes in concentration $\Delta[\mathrm{A}]$ that occur during a short time interval Δt. Sometimes it can be difficult to obtain sufficiently precise experimental data for these small changes. An alternative is to use an **integrated rate law,** which expresses the concentration of a species directly as a function of the time. For any simple rate expression, a corresponding integrated rate law can be obtained.

FIRST-ORDER REACTIONS

Consider again the reaction

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

whose rate law has been determined experimentally to be

$$\text{rate} = -\frac{d[N_2O_5]}{dt} = k[N_2O_5]$$

This is a first-order reaction. If we let $[N_2O_5] = c$, a function of time, we have

$$\frac{dc}{dt} = -kc$$

We seek a function whose slope at every time is proportional to the value of the function itself. This function can be found through the use of calculus. Separating the variables (with concentration c on the left and time t on the right) gives

$$\frac{1}{c}\,dc = -k\,dt$$

Integrating from an initial concentration c_0 at time $t = 0$ to a concentration c at time t (see Appendix C, Section C.5) gives

$$\int_{c_0}^{c} \frac{1}{c}\,dc = -k\int_0^t dt$$

$$\ln c - \ln c_0 = -kt$$

$$\ln (c/c_0) = -kt$$

$$\boxed{c = c_0\, e^{-kt}} \qquad [18.2]$$

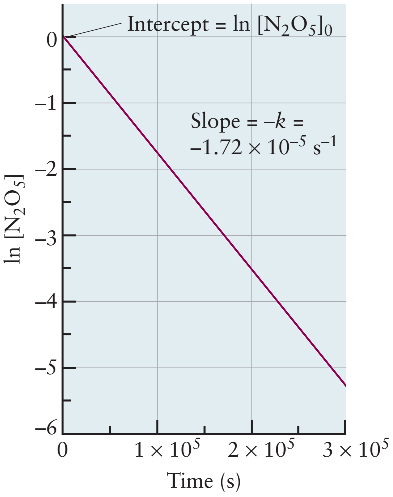


FIGURE 18.5 In a first-order reaction such as the decomposition of N_2O_5, a graph of the natural logarithm of the concentration against time is a straight line, the negative of whose slope gives the rate constant for the reaction.

The concentration falls off exponentially with time. For a first-order reaction, a plot of ln c against t is a straight line with slope $-k$ (Fig. 18.5).

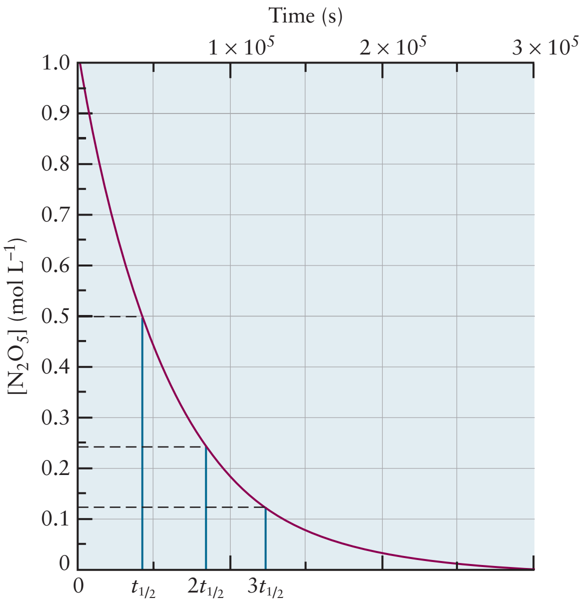
A useful concept in discussions of first-order reactions is the **half-life** $t_{1/2}$—the time it takes for the original concentration c_0 to be reduced to half its value, $c_0/2$. Setting $c = c_0/2$ gives

$$\ln\left(\frac{c}{c_0}\right) = \ln\left(\frac{c_0/2}{c_0}\right) = -\ln 2 = -kt_{1/2}$$

$$\boxed{t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k}} \qquad [18.3]$$

If k has units of s^{-1}, (ln 2)/k is the half-life in seconds. During each half-life, the concentration of A falls to half its value again (Fig. 18.6).

FIGURE 18.6 The same data as in Figure 18.5 are graphed in a concentration-versus-time picture. The half-life $t_{1/2}$ is the time it takes for the concentration to be reduced to half its initial value. In two half-lives, the concentration falls to one quarter of its initial value.



EXAMPLE 18.4

(a) What is the rate constant k for the first-order decomposition of $N_2O_5(g)$ at 25°C if the half-life of $N_2O_5(g)$ at that temperature is 4.03×10^4 s?

(b) What percentage of the N_2O_5 molecules will *not* have reacted after one day?

SOLUTION

(a)
$$t_{1/2} = \frac{\ln 2}{k} = 4.03 \times 10^4 \text{ s}$$

Solving for the rate constant k gives

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.6931}{4.03 \times 10^4 \text{ s}} = 1.72 \times 10^{-5} \text{ s}^{-1}$$

(b) From the integrated rate law for a first-order reaction,

$$\frac{c}{c_0} = e^{-kt}$$

Putting in the value for k and setting t to 1 day $= 8.64 \times 10^4$ s gives

$$\frac{c}{c_0} = \exp\left[-(1.72 \times 10^{-5} \text{ s}^{-1})(8.64 \times 10^4 \text{ s})\right]$$
$$= e^{-1.49} = 0.226$$

Therefore, 22.6% of the molecules will not yet have reacted after one day.

Related Problems: 11, 12

SECOND-ORDER REACTIONS

Integrated rate laws can be obtained for reactions of other orders. The observed rate of the reaction

$$2\,NO_2(g) \longrightarrow 2\,NO(g) + O_2(g)$$

is second order in $[NO_2]$:

$$\text{rate} = -\frac{1}{2}\frac{d[NO_2]}{dt} = k[NO_2]^2$$

Writing $[NO_2] = c$ and multiplying both sides of the equation by -1 gives

$$\frac{dc}{dt} = -2kc^2$$

$$\frac{1}{c^2}\,dc = -2k\,dt$$

Integrating this from the initial concentration c_0 at time 0 to c at time t gives

$$\int_{c_0}^{c}\frac{1}{c^2}\,dc = -2k\int_0^t dt$$

$$-\frac{1}{c} + \frac{1}{c_0} = -2kt$$

$$\boxed{\frac{1}{c} = \frac{1}{c_0} + 2kt} \qquad [18.4]$$

For such a second-order reaction, a plot of $1/c$ against t is linear (Fig. 18.7). The factor 2 multiplying kt in this expression arises from the stoichiometric coefficient 2 for NO_2 in the balanced equation for the specific example reaction. For other second-order reactions with different stoichiometric coefficients for the reactant (see the thermal decomposition of ethane described on page 755), we must modify the integrated rate law accordingly.

The concept of half-life has little use for second-order reactions. Setting $[NO_2]$ equal to $[NO_2]_0/2$ in the preceding equation and solving for t gives

$$\frac{2}{[NO_2]} = 2kt_{1/2} + \frac{1}{[NO_2]_0}$$

$$t_{1/2} = \frac{1}{2k[NO_2]_0}$$

For second-order reactions, the half-life is not a constant; it depends on the initial concentration.

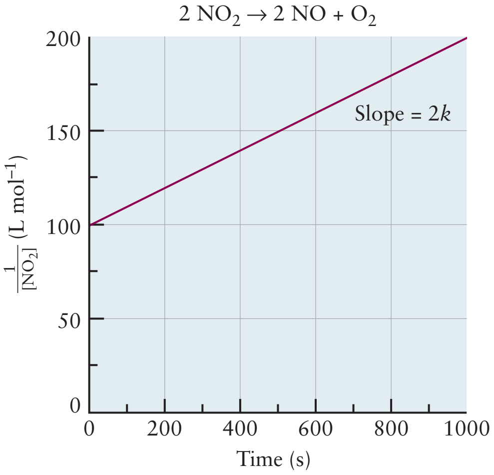


FIGURE 18.7 For a second-order reaction such as $2\,NO_2 \longrightarrow 2\,NO + O_2$, a graph of the reciprocal of the concentration against time is a straight line with slope $2k$.

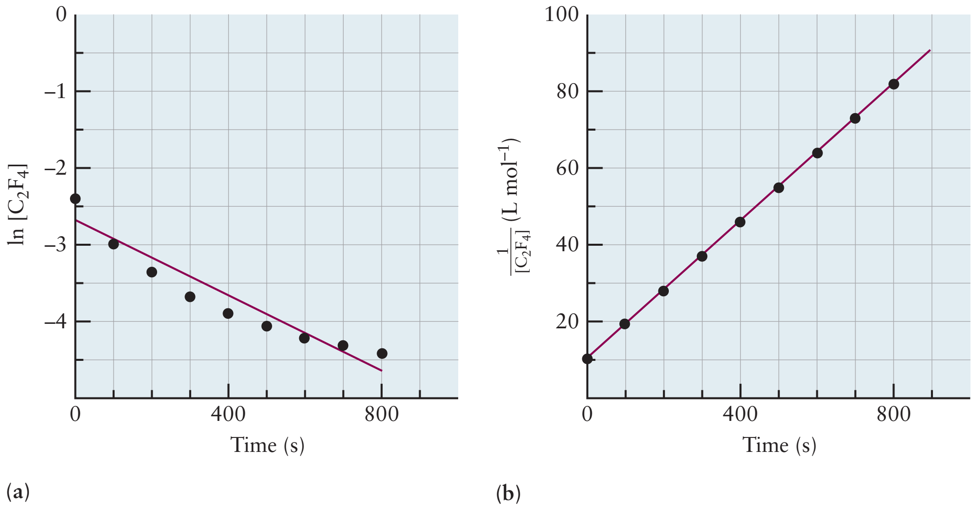


FIGURE 18.8 For the reaction in Example 18.5, (a) plotting the logarithm of the concentration of C_2F_4 against time tests for first-order kinetics and (b) plotting the reciprocal of the concentration of C_2F_4 against time tests for second-order kinetics. It is clear that the assumption of first-order kinetics does not fit the data as well; no straight line will pass through the data.

EXAMPLE 18.5

The dimerization of tetrafluoroethylene (C_2F_4) to octafluorocyclobutane (C_4F_8) is second order in the reactant C_2F_4, and at 450 K its rate constant is $k = 0.0448$ L mol^{-1} s^{-1}. If the initial concentration of C_2F_4 is 0.100 mol L^{-1}, what will its concentration be after 205 s?

SOLUTION

For this second-order reaction,

$$\frac{1}{c} - \frac{1}{c_0} = 2kt$$

Solving for the concentration c after a time $t = 205$ s gives

$$\frac{1}{c} = (2)(0.0448 \text{ L mol}^{-1} \text{ s}^{-1})(205 \text{ s}) + \frac{1}{0.100 \text{ mol L}^{-1}} = 28.4 \text{ L mol}^{-1}$$

$$c = 3.53 \times 10^{-2} \text{ mol L}^{-1}$$

Related Problems: 15, 16

In a real experimental study the reaction order is usually not known. In such a case we try several plots to find the one that best fits the data (Fig. 18.8).

18.3 Reaction Mechanisms

Many reactions do not occur in a single step, but rather proceed through a sequence of steps to arrive at the products. Each step is called an **elementary reaction** and occurs through the collisions of atoms, ions, or molecules. The rate expression for an overall reaction cannot be derived from the stoichiometry of the balanced equation, and must be determined experimentally. But the rate of an elementary reaction *is* directly proportional to the product of the concentrations of the reacting species, each raised to a power equal to its coefficient in the balanced elementary equation.

Elementary Reactions

A **unimolecular** elementary reaction involves only a single reactant molecule. An example is the dissociation of energized N_2O_5 molecules in the gas phase:

$$N_2O_5^*(g) \longrightarrow NO_2(g) + NO_3(g)$$

The asterisk indicates that the N_2O_5 molecules have far more than ground state energy. This step is unimolecular and has the rate expression

$$\text{rate} = k[N_2O_5^*]$$

An important class of unimolecular reactions is the decay of radioactive nuclei, considered in Chapter 19.

The most common type of elementary reaction involves the collision of two atoms, ions, or molecules and is called **bimolecular.** An example is the reaction

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

The frequency at which a given NO molecule collides with ozone molecules is proportional to the concentration of ozone: If there are twice as many ozone molecules per unit volume, each NO molecule will undergo twice as many collisions as it moves through space, and ozone will react twice as rapidly. The rate of collisions of *all* the NO molecules in the container is proportional to the concentration of NO as well, so the rate law of a bimolecular reaction like this one has the form

$$\text{rate} = k[NO][O_3]$$

A **termolecular** reaction step involves the simultaneous collision of three molecules, which is a much less likely event. An example is the recombination of iodine atoms in the gas phase to form iodine molecules. So much energy is released in forming the I—I bond that the molecule would simply fly apart as soon as it was formed if the event were a binary collision. A third atom or molecule is necessary to take away some of the excess energy. If iodine recombination takes place in the presence of a sufficiently high concentration of an inert gas such as argon, termolecular reactions

$$I(g) + I(g) + Ar(g) \longrightarrow I_2(g) + Ar(g)$$

occur in which the argon atom leaves with more kinetic energy than it had initially. The rate law for this termolecular reaction is

$$\text{rate} = k[I]^2[Ar]$$

Elementary reactions involving collisions of four or more molecules are not observed, and even termolecular collisions are rare if other pathways are possible.

Elementary reactions in liquid solvents involve encounters of solute species with one another. If the solution is ideal, the rates of these processes are proportional to the product of the concentrations of the solute species involved. Solvent molecules are always present and may affect the reaction, even though they do not appear in the rate expression because the solvent concentration cannot be varied appreciably. A reaction such as the recombination of iodine atoms occurs readily in a liquid. It appears to be second order with rate law

$$\text{rate} = k[I]^2$$

only because the third body involved is a solvent molecule. In the same way, a reaction between a solvent molecule and a solute molecule appears to be unimolecular, and only the concentration of solute molecules enters the rate expression for that step.

Reaction Mechanisms

A **reaction mechanism** is a detailed sequence of elementary reactions, with their rates, that are combined to yield the overall reaction. It is often possible to write several reaction mechanisms, each of which is consistent with a given overall reaction. One of the goals of chemical kinetics is to use the observed rate of a reaction to choose among various conceivable reaction mechanisms.

The gas-phase reaction of nitrogen dioxide with carbon monoxide provides a good example of a reaction mechanism. The generally accepted mechanism at low temperatures has two steps, both bimolecular:

$$NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g) \qquad \text{(slow)}$$

$$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g) \qquad \text{(fast)}$$

For any reaction mechanism, combining the steps must give the overall reaction. When each elementary step occurs the same number of times in the course of the reaction, the chemical equations can simply be added. (If one step occurs twice as often as the others, it must be multiplied by 2 before the elementary reactions are added.) In this case, we add the two chemical equations to give

$$2\ NO_2(g) + NO_3(g) + CO(g) \longrightarrow NO_3(g) + NO(g) + NO_2(g) + CO_2(g)$$

Canceling out the NO_3 and one molecule of NO_2 from each side leads to

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

A **reaction intermediate** (here, NO_3) is a chemical species that is formed and consumed in the reaction but does not appear in the overall balanced chemical equation. One of the major challenges in chemical kinetics is to identify intermediates, which are often so short-lived that they are difficult to detect directly.

EXAMPLE 18.6

Consider the following reaction mechanism:

$$Cl_2(g) \longrightarrow 2\ Cl(g)$$

$$Cl(g) + CHCl_3(g) \longrightarrow HCl(g) + CCl_3(g)$$

$$CCl_3(g) + Cl(g) \longrightarrow CCl_4(g)$$

(a) What is the molecularity of each elementary step?

(b) Write the overall equation for the reaction.

(c) Identify the reaction intermediate(s).

SOLUTION

(a) The first step is unimolecular, and the other two are bimolecular.

(b) Adding the three steps gives

$$Cl_2(g) + 2\ Cl(g) + CHCl_3(g) + CCl_3(g) \longrightarrow 2\ Cl(g) + HCl(g) + CCl_3(g) + CCl_4(g)$$

The two species that appear in equal amounts on both sides cancel out to leave

$$Cl_2(g) + CHCl_3(g) \longrightarrow HCl(g) + CCl_4(g)$$

(c) The two reaction intermediates are Cl and CCl_3.

Related Problems: 21, 22

Kinetics and Chemical Equilibrium

There is a direct connection between the rates for the elementary steps in a chemical reaction mechanism and the overall equilibrium constant *K*. To see this connection, consider the reaction

$$2\ NO(g) + 2\ H_2(g) \rightleftharpoons N_2(g) + 2\ H_2O(g)$$

This reaction is believed to occur in a three-step process involving N_2O_2 and N_2O as intermediates:

$$NO(g) + NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} N_2O_2(g)$$

$$N_2O_2(g) + H_2(g) \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} N_2O(g) + H_2O(g)$$

$$N_2O(g) + H_2(g) \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} N_2(g) + H_2O(g)$$

These elementary reactions are shown as equilibria, so the reverse reactions (from products to reactants) are included here as well; k_1, k_2, and k_3 are the rate constants for the forward elementary steps, and k_{-1}, k_{-2}, and k_{-3} are the rate constants for the corresponding reverse reactions.

We now invoke the principle of **detailed balance,** which states that at equilibrium the rate of *each* elementary process is balanced by (equal to) the rate of its reverse process. For the preceding mechanism we conclude that

$$k_1[NO]^2_{eq} = k_{-1}[N_2O_2]_{eq}$$

$$k_2[N_2O_2]_{eq}[H_2]_{eq} = k_{-2}[N_2O]_{eq}[H_2O]_{eq}$$

$$k_3[N_2O]_{eq}[H_2]_{eq} = k_{-3}[N_2]_{eq}[H_2O]_{eq}$$

The equilibrium constants[1] K_1, K_2, and K_3 for the elementary reactions are equal to the ratio of the forward and reverse reaction rate constants:

$$K_1 = \frac{[N_2O_2]_{eq}}{[NO]^2_{eq}} = \frac{k_1}{k_{-1}}$$

$$K_2 = \frac{[N_2O]_{eq}[H_2O]_{eq}}{[N_2O_2]_{eq}[H_2]} = \frac{k_2}{k_{-2}}$$

$$K_3 = \frac{[N_2]_{eq}[H_2O]_{eq}}{[N_2O]_{eq}[H_2]_{eq}} = \frac{k_3}{k_{-3}}$$

The steps of the mechanism are now added together to obtain the overall reaction. Recall from Section 14.4 that when reactions are added, their equilibrium constants are multiplied. Therefore, the overall equilibrium constant K is

$$K = K_1K_2K_3 = \frac{k_1k_2k_3}{k_{-1}k_{-2}k_{-3}} = \frac{[N_2O_2]_{eq}[N_2O]_{eq}[H_2O]_{eq}[N_2]_{eq}[H_2O]_{eq}}{[NO]^2_{eq}[N_2O_2]_{eq}[H_2]_{eq}[N_2O]_{eq}[H_2]_{eq}}$$

$$= \frac{[H_2O]^2_{eq}[N_2]_{eq}}{[NO]^2_{eq}[H_2]^2_{eq}}$$

The concentrations of the intermediates N_2O_2 and N_2O cancel out, giving the usual expression of the mass-action law.

This result can be generalized to any reaction mechanism. The product of the forward rate constants for the elementary reactions divided by the product of the reverse rate constants is always equal to the equilibrium constant of the overall reaction. If there are several possible mechanisms for a given reaction (which might involve intermediates other than N_2O_2 and N_2O), their forward and reverse rate constants will all be consistent in this way with the equilibrium constant of the overall reaction.

---

[1] Thermodynamic equilibrium constants are dimensionless because they are expressed in terms of activities rather than partial pressure or concentration. The convention in chemical kinetics is to use concentrations rather than activities, even for gaseous species. Therefore, the equilibrium constants K_1, K_2, and K_3 introduced here are the empirical equilibrium constants K_c described briefly in Section 14.2. These constants are not dimensionless and must be multiplied by the concentration of the reference state, $c_{ref} = RT/P_{ref}$, raised to the appropriate power to be made equal to the thermodynamic equilibrium constant. Nevertheless, to maintain consistency with the conventions of chemical kinetics, such constants as K_1, K_2, and K_3 are referred to as equilibrium constants in this section and are written without the subscript c.

18.4 Reaction Mechanisms and Rate

In many reaction mechanisms, one step is significantly slower than all the others; this step is called the **rate-determining step.** Because an overall reaction can occur only as fast as its slowest step, that step is crucial in determining the rate of the reaction. This is analogous to the flow of automobile traffic on a highway which has a slowdown at some point. The rate at which cars can complete a trip down the full length of the highway (in cars per minute) is approximately equal to the rate at which they pass through the bottleneck.

If the rate-determining step is the first one, the analysis is particularly simple. An example is the reaction

$$2\ \mathrm{NO_2}(g) + \mathrm{F_2}(g) \longrightarrow 2\ \mathrm{NO_2F}(g)$$

for which the experimental rate law is

$$\text{rate} = k_{\text{obs}}[\mathrm{NO_2}][\mathrm{F_2}]$$

A possible mechanism for the reaction is

$$\mathrm{NO_2}(g) + \mathrm{F_2}(g) \xrightarrow{k_1} \mathrm{NO_2F}(g) + \mathrm{F}(g) \qquad \text{(slow)}$$

$$\mathrm{NO_2}(g) + \mathrm{F}(g) \xrightarrow{k_2} \mathrm{NO_2F}(g) \qquad \text{(fast)}$$

The first step is slow and determines the rate, $k_1[\mathrm{NO_2}][\mathrm{F_2}]$, in agreement with the observed rate expression. The subsequent fast step does not affect the reaction rate because fluorine atoms react with $\mathrm{NO_2}$ almost as soon as they are produced.

Mechanisms in which the rate-determining step occurs after one or more fast steps are often signaled by a reaction order greater than 2, by a nonintegral reaction order, or by an inverse concentration dependence on one of the species taking part in the reaction. An example is the reaction

$$2\ \mathrm{NO}(g) + \mathrm{O_2}(g) \longrightarrow 2\ \mathrm{NO_2}(g)$$

for which the experimental rate law is

$$\text{rate} = k_{\text{obs}}[\mathrm{NO}]^2[\mathrm{O_2}]$$

One possible mechanism would be a single-step termolecular reaction of two NO molecules with one $\mathrm{O_2}$ molecule. This would be consistent with the form of the rate expression, but termolecular collisions are rare, and if there is an alternative pathway it is usually followed.

One such alternative is the two-step mechanism

$$\mathrm{NO}(g) + \mathrm{NO}(g) \overset{k_1}{\rightleftarrows} \mathrm{N_2O_2}(g) \qquad \text{(fast equilibrium)}$$

$$\mathrm{N_2O_2}(g) + \mathrm{O_2}(g) \overset{k_2}{\rightleftarrows} 2\ \mathrm{NO_2}(g) \qquad \text{(slow)}$$

Because the slow step determines the overall rate, we can write

$$\text{rate} = k_2[\mathrm{N_2O_2}][\mathrm{O_2}]$$

The concentration of a reactive intermediate such as $\mathrm{N_2O_2}$ cannot be varied at will. Because the $\mathrm{N_2O_2}$ reacts only slowly with $\mathrm{O_2}$, the reverse reaction (to 2 NO) is possible and must be taken into account. In fact, it is reasonable to assume that all of the elementary reactions that occur *before* the rate-determining step are in equilibrium, with the forward and reverse reactions occurring at the same rate. In this case, we have

$$\frac{[\mathrm{N_2O_2}]}{[\mathrm{NO}]^2} = \frac{k_1}{k_{-1}} = K_1$$

$$[\mathrm{N_2O_2}] = K_1[\mathrm{NO}]^2$$

$$\text{rate} = k_2K_1[\mathrm{NO}]^2[\mathrm{O_2}]$$

This result is consistent with the observed reaction order, with $k_2k_1 = k_{\text{obs}}$.

EXAMPLE 18.7

In basic aqueous solution the reaction

$$I^- + OCl^- \longrightarrow Cl^- + OI^-$$

follows a rate law that is consistent with the following mechanism:

$$OCl^-(aq) + H_2O(\ell) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} HOCl(aq) + OH^-(aq) \qquad \text{(fast equilibrium)}$$

$$I^-(aq) + HOCl(aq) \xrightarrow{k_2} HOI(aq) + Cl^-(aq) \qquad \text{(slow)}$$

$$OH^-(aq) + HOI(aq) \xrightarrow{k_3} H_2O(\ell) + OI^-(aq) \qquad \text{(fast)}$$

What rate law is predicted by this mechanism?

SOLUTION

The rate is determined by the slowest elementary step, the second one:

$$\text{rate} = k_2[I^-][HOCl]$$

But, the HOCl is in equilibrium with OCl^- and OH^- due to the first step:

$$\frac{[HOCl][OH^-]}{[OCl^-]} = K_1 = \frac{k_1}{k_{-1}}$$

Solving this for [HOCl] and inserting it into the previous expression gives the prediction

$$\text{rate} = k_2 K_1 \frac{[I^-][OCl^-]}{[OH^-]}$$

which is, in fact, the experimentally observed rate law.

Related Problems: 25, 26, 27, 28, 29, 30

The rate law of the foregoing example depends on the inverse of the concentration of OH^- ion. Such a form is often a clue that a rapid equilibrium occurs in the first steps of a reaction, preceding the rate-determining step. Fractional orders of reaction provide a similar clue, as in the reaction of H_2 with Br_2 to form HBr,

$$H_2 + Br_2 \longrightarrow 2\ HBr$$

for which the initial reaction rate (before very much HBr builds up) is

$$\text{rate} = k_{\text{obs}}[H_2][Br_2]^{1/2}$$

How can such a fractional power appear? One reaction mechanism that predicts this rate law is

$$Br_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Br + Br + M \qquad \text{(fast equilibrium)}$$

$$Br + H_2 \xrightarrow{k_2} HBr + H \qquad \text{(slow)}$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br \qquad \text{(fast)}$$

Here M stands for a second molecule that does not react but that supplies the energy to break up the bromine molecules. For such a mechanism the reaction rate is determined by the slow step:

$$\text{rate} = k_2[Br][H_2]$$

However, [Br] is fixed by the establishment of equilibrium in the first reaction,

$$\frac{[Br]^2}{[Br_2]} = K_1 = \frac{k_1}{k_{-1}}$$

so

$$[\mathrm{Br}] = K_1^{1/2}[\mathrm{Br_2}]^{1/2}$$

The rate expression predicted by this mechanism is thus

$$\text{rate} = k_2K_1^{1/2}[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}$$

This is in accord with the observed fractional power in the rate law. On the other hand, the simple bimolecular mechanism

$$\mathrm{H_2} + \mathrm{Br_2} \xrightarrow{k_1} 2\ \mathrm{HBr} \qquad \text{(slow)}$$

predicts a rate law:

$$\text{rate} = k_1[\mathrm{H_2}][\mathrm{Br_2}]$$

This disagrees with the observed rate law, so it can be ruled out as the major contributor to the measured rate.

This discussion shows that deducing a rate law from a proposed mechanism is relatively straightforward, but doing the reverse is much harder. In fact, several competing mechanisms often give rise to the same rate law, and only some independent type of measurement can distinguish between them. A proposed reaction mechanism cannot be proven to be correct if its predictions agree with an experimental rate law, but it can be proven wrong if its predictions disagree with the experimental results.

A classic example is the reaction

$$\mathrm{H_2} + \mathrm{I_2} \longrightarrow 2\ \mathrm{HI}$$

for which the observed rate law is

$$\text{rate} = k_{\text{obs}}[\mathrm{H_2}][\mathrm{I_2}]$$

(Contrast this with the rate law already given for the analogous reaction of H_2 with Br_2.) This is one of the earliest and most extensively studied reactions in chemical kinetics, and until 1967 it was widely believed to occur as a one-step elementary reaction. At that time J. H. Sullivan investigated the effect of illuminating the reacting sample with light, which splits some of the I_2 molecules into iodine atoms. If the mechanism we proposed for H_2 and Br_2 is correct here as well, the effect of the light on the reaction should be small because it leads only to a small decrease in the I_2 concentration.

Instead, Sullivan observed a dramatic *increase* in the rate of reaction under illumination, which could be explained only by the participation of iodine *atoms* in the reaction mechanism. One such mechanism is

$$\mathrm{I_2} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{I} + \mathrm{I} + \mathrm{M} \qquad \text{(fast equilibrium)}$$

$$\mathrm{H_2} + \mathrm{I} + \mathrm{I} \xrightarrow{k_2} 2\ \mathrm{HI} \qquad \text{(slow)}$$

for which the rate law is

$$\text{rate} = k_2[\mathrm{H_2}][\mathrm{I}]^2 = k_2K_1[\mathrm{H_2}][\mathrm{I_2}]$$

This mechanism gives the same rate law that is observed experimentally, and it is consistent with the effect of light on the reaction. The other reaction mechanism also appears to contribute significantly to the overall rate.

This example illustrates the hazards of trying to determine reaction mechanisms from rate laws: several mechanisms can fit any given empirical rate law, and it is always possible that a new piece of information suggesting a different mechanism will be found. The problem is that, under ordinary conditions, reaction intermediates cannot be isolated and studied like the reactants and products. This situation is changing with the development of experimental techniques that allow the direct study of the transient intermediates that form in small concentration during the course of a chemical reaction.

The Steady-State Approximation

In some reaction mechanisms there is no single step that is much slower than the others, so the methods discussed so far cannot predict the rate law. In such cases we use the **steady-state approximation,** which states that the concentrations of reactive intermediates remain nearly constant through most of the reaction.

To illustrate this approximation, let's examine the mechanism proposed by F. A. Lindemann for the dissociation of molecules in the gas phase. A molecule such as N_2O_5 undergoes collisions with neighboring molecules M, where M can stand for another N_2O_5 molecule or for an inert gas such as argon. Through such collisions the N_2O_5 molecule can become excited (or activated) to a state indicated by $N_2O_5^*$:

$$N_2O_5(g) + M(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_5^*(g) + M(g)$$

The reverse process, with rate constant k_{-1}, is also indicated because the activated molecule can be deactivated by collisions with other molecules. The second step is the unimolecular decomposition of $N_2O_5^*$:

$$N_2O_5^*(g) \xrightarrow{k_2} NO_3(g) + NO_2(g)$$

Subsequent reaction steps to form O_2 and NO_2 from NO_3 occur rapidly and do not affect the measured rate:

$$NO_3(g) + NO_2(g) \xrightarrow{k_3} NO(g) + NO_2(g) + O_2(g) \qquad \text{(fast)}$$

$$NO_3(g) + NO(g) \xrightarrow{k_4} 2\ NO_2(g) \qquad \text{(fast)}$$

The $N_2O_5^*$ is a reactive intermediate; it is produced at a rate $k_1[N_2O_5][M]$ from collisions of N_2O_5 molecules with other molecules and is lost at a rate $k_{-1}[N_2O_5^*][M]$ due to deactivation and at a rate $k_{-2}[N_2O_5^*][M]$ due to dissociation. The net rate of change of $[N_2O_5^*]$ is then

$$\frac{d[N_2O_5^*]}{dt} = k_1[N_2O_5][M] - k_{-1}[N_2O_5^*][M] - k_2[N_2O_5^*]$$

At the beginning of the reaction, $[N_2O_5^*] = 0$, but this concentration builds up after a short time to a small value. The steady-state approximation consists of the assumption that after this short time the rates of production and loss of $N_2O_5^*$ become equal, and

$$\frac{d[N_2O_5^*]}{dt} = 0$$

The steady-state concentration of $[N_2O_5^*]$ persists practically unchanged throughout most of the course of the reaction.

Setting the net rate of change of the $N_2O_5^*$ concentration to 0 gives

$$\frac{d[N_2O_5^*]}{dt} = 0 = k_1[N_2O_5][M] - k_{-1}[N_2O_5^*][M] - k_2[N_2O_5^*]$$

Solving for $[N_2O_5^*]$ gives

$$[N_2O_5^*](k_2 + k_{-1}[M]) = k_1[N_2O_5][M]$$

$$[N_2O_5^*] = \frac{k_1[N_2O_5][M]}{k_2 + k_{-1}[M]}$$

The rate of the overall reaction $N_2O_5 \longrightarrow 2\ NO_2 + \frac{1}{2}\ O_2$ is

$$\text{rate} = \frac{1}{2}\frac{d[NO_2]}{dt} = k_2[N_2O_5^*] = \frac{k_1k_2[N_2O_5][M]}{k_2 + k_{-1}[M]}$$

This expression has two limiting cases:

1. *Low pressure* When [M] is small enough, $k_2 \gg k_{-1}[\mathrm{M}]$ and we can use the approximation

$$\text{rate} = k_1[\mathrm{N_2O_5}][\mathrm{M}] \qquad \text{(second order)}$$

This same result would be found by assuming the first step to be rate-determining.

2. *High pressure* When [M] is large enough, $k_{-1}[\mathrm{M}] \gg k_2$ and we can use the approximation

$$\text{rate} = \frac{k_1}{k_{-1}} k_2[\mathrm{N_2O_5}] \qquad \text{(first order)}$$

This same result would be found by assuming the second step to be rate-determining.

The steady-state approximation is a more general approach than those considered earlier and can be used when no single rate-determining step exists.

Chain Reactions

A **chain reaction** proceeds through a series of elementary steps, some of which are repeated many times. Chain reactions have three stages: (1) **initiation,** in which two or more reactive intermediates are generated; (2) **propagation,** in which products are formed but reactive intermediates are continuously regenerated; and (3) **termination,** in which two intermediates combine to give a stable product.

An example of a chain reaction is the reaction of methane with fluorine to give CH_3F and HF:

$$\mathrm{CH_4}(g) + \mathrm{F_2}(g) \longrightarrow \mathrm{CH_3F}(g) + \mathrm{HF}(g)$$

Although in principle this reaction could occur through a one-step bimolecular process, that route turns out to be too slow to contribute significantly under normal reaction conditions. Instead, the mechanism involves a chain reaction of the following type:

$$\mathrm{CH_4}(g) + \mathrm{F_2}(g) \longrightarrow \mathrm{CH_3}(g) + \mathrm{HF}(g) + \mathrm{F}(g) \qquad \text{(initiation)}$$

$$\mathrm{CH_3}(g) + \mathrm{F_2}(g) \longrightarrow \mathrm{CH_3F}(g) + \mathrm{F}(g) \qquad \text{(propagation)}$$

$$\mathrm{CH_4}(g) + \mathrm{F}(g) \longrightarrow \mathrm{CH_3}(g) + \mathrm{HF}(g) \qquad \text{(propagation)}$$

$$\mathrm{CH_3}(g) + \mathrm{F}(g) + \mathrm{M}(g) \longrightarrow \mathrm{CH_3F}(g) + \mathrm{M}(g) \qquad \text{(termination)}$$

In the initiation step, two reactive intermediates (CH_3 and F) are produced. During the propagation steps, these intermediates are not used up while reactants (CH_4 and F_2) are being converted to products (CH_3F and HF). The propagation steps can be repeated again and again, until eventually two reactive intermediates come together in a termination step. As we see in Chapter 23, chain reactions are important in building up long-chain molecules called polymers.

The chain reaction just considered proceeds at a constant rate, because each propagation step both uses up and produces a reactive intermediate. The concentrations of the reactive intermediates remain approximately constant and are determined by the rates of chain initiation and termination. Another type of chain reaction is possible in which the number of reactive intermediates increases during one or more propagation steps. This is called a **branching chain reaction.** An example is the reaction of oxygen with hydrogen. The mechanism is complex and can be initiated in various ways, leading to the formation of several reactive intermediates such as O, H, and OH. Some propagation steps are of the type already seen for CH_4 and F_2, such as

$$\mathrm{OH}(g) + \mathrm{H_2}(g) \longrightarrow \mathrm{H_2O}(g) + \mathrm{H}(g)$$

in which one reactive intermediate (OH) is used up and one (H) is produced. Other propagation steps are branching:

$$\mathrm{H}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{OH}(g) + \mathrm{O}(g)$$

$$\mathrm{O}(g) + \mathrm{H_2}(g) \longrightarrow \mathrm{OH}(g) + \mathrm{H}(g)$$

In these steps, each reactive intermediate used up causes the generation of two others. This leads to rapid growth in the number of reactive species, speeding the rate further and possibly causing an explosion. Branching chain reactions are critical in the fission of uranium (see Chapter 19).

18.5 Effect of Temperature on Reaction Rates

The first four sections of this chapter describe the experimental determination of rate laws and their relation to assumed mechanisms for chemical reactions. Now we have to find out what determines the actual magnitudes of rate constants (either for elementary reactions or for overall rates of multistep reactions), and how temperature affects reaction rates. To consider these matters, it is necessary to connect molecular collision rates to the rates of chemical reactions. We limit the discussion to gas-phase reactions, for which the kinetic theory of Chapter 9 is applicable.

Gas-Phase Reaction Rate Constants

In Section 9.8, we applied the kinetic theory of gases to estimate the frequency of collisions between a particular molecule and other molecules in a gas. In Example 9.14, we calculated this frequency to be $4.1 \times 10^9 \text{ s}^{-1}$ under room conditions for a typical small molecule such as oxygen. If every collision led to reaction, the reaction would be practically complete in about 10^{-9} s. Some reactions do proceed at rates almost this high. An example is the bimolecular reaction between two CH_3 radicals to give ethane, C_2H_6,

$$2\ \mathrm{CH_3} \longrightarrow \mathrm{C_2H_6}$$

for which the observed rate constant is $1 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$. For initial pressure of CH_3 near 1 atm at 25°C, the concentration initially is about 0.04 M. The second-order integrated rate law from Section 18.2 predicts that the concentration would drop to 0.02 M after a period of 10^{-9} s. But, reaction rates that are much lower—by factors of 10^{12} or more—are common. The naive idea that "to collide is to react" clearly must be modified if we are to understand these lower rates.

We find a clue in the observed temperature dependence of reaction rate constants. The rates of many reactions increase extremely rapidly as temperature increases; typically a 10°C rise in temperature may double the rate. In 1889 Svante Arrhenius suggested that rate constants vary exponentially with inverse temperature,

$$\boxed{k = Ae^{-E_a/RT}} \qquad [18.5]$$

where E_a is a constant with dimensions of energy and A is a constant with the same dimensions as k. Taking the natural logarithm of this equation gives

$$\boxed{\ln k = \ln A - \frac{E_a}{RT}} \qquad [18.6]$$

So a plot of $\ln k$ against $1/T$ should be a straight line with slope $-E_a/R$ and intercept $\ln A$. Many rate constants do show just this kind of temperature dependence (Fig. 18.9).

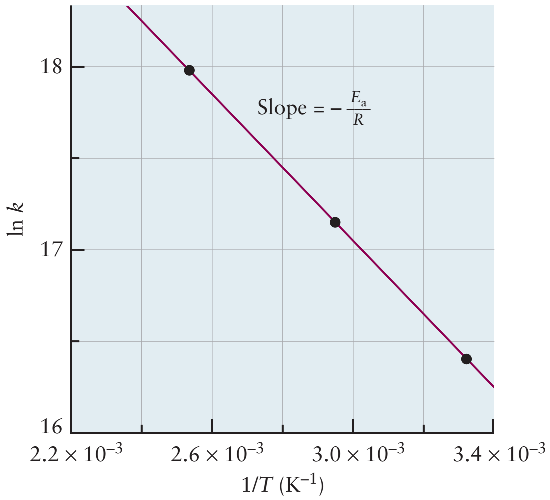


FIGURE 18.9 An Arrhenius plot of ln k against $1/T$ for the reaction of benzene vapor with oxygen atoms. An extrapolation to $1/T = 0$ gives the constant ln A from the intercept of this line.

EXAMPLE 18.8

The decomposition of hydroxylamine (NH_2OH) in the presence of oxygen follows the rate law

$$-\frac{d[NH_2OH]}{dt} = k_{obs}[NH_2OH][O_2]$$

where k_{obs} is 0.237×10^{-4} L mol^{-1} s^{-1} at 0°C and 2.64×10^{-4} L mol^{-1} s^{-1} at 25°C. Calculate E_a and the factor A for this reaction.

SOLUTION

Let us write the Arrhenius equation at two different temperatures T_1 and T_2:

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \text{and} \quad \ln k_2 = \ln A - \frac{E_a}{RT_2}$$

If the first equation is subtracted from the second, the term ln A cancels out, leaving

$$\ln k_2 - \ln k_1 = \ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

which can be solved for E_a. In the present case, $T_1 = 273$ K and $T_2 = 298$ K; therefore,

$$\ln \frac{2.64 \times 10^{-4}}{0.237 \times 10^{-4}} = \frac{-E_a}{8.315 \text{ J K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{298 \text{ K}} - \frac{1}{273 \text{ K}}\right)$$

$$2.410 = \frac{E_a}{8.315 \text{ J K}^{-1} \text{ mol}^{-1}}(3.07 \times 10^{-4} \text{ K}^{-1})$$

$$E_a = 6.52 \times 10^4 \text{ J mol}^{-1} = 65.2 \text{ kJ mol}^{-1}$$

Now that E_a is known, the constant A can be calculated by using data at either temperature. At 273 K,

$$\ln A = \ln k_1 + \frac{E_a}{RT}$$

$$= \ln(0.237 \times 10^{-4}) + \frac{6.52 \times 10^4 \text{ J mol}^{-1}}{(8.315 \text{ J K}^{-1} \text{ mol}^{-1})(273 \text{ K})}$$

$$= -10.65 + 28.73 = 18.08$$

$$A = e^{18.08} = 7.1 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-}$$

We could determine E_a and A more accurately from measurements at a series of temperatures and a least-squares fit to a plot such as that in Figure 18.9.

Related Problems: 35, 36

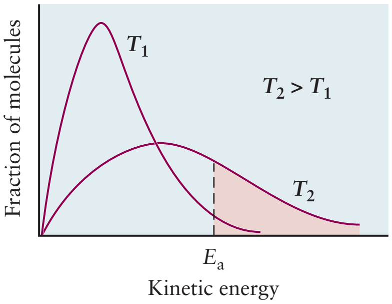


FIGURE 18.10 The Maxwell–Boltzmann distribution of molecular kinetic energies, showing the effect of temperature on the fraction of molecules having large enough kinetic energies to react. This figure shows only translational energy; internal vibrational and rotational energy also promote reactions.

Arrhenius believed that for molecules to react upon collision they must become "activated," so the parameter E_a came to be known as the **activation energy.** His ideas were refined by later scientists. In 1915 A. Marcelin pointed out that, while molecules make many collisions, not all collisions are reactive. Only those collisions for which the collision energy (i.e., the relative translational kinetic energy of the colliding molecules) exceeds some critical energy result in reaction. Thus, Marcelin gave a dynamic interpretation for the activation energy inferred from reaction rates.

The strong temperature dependence of rate constants, described by the Arrhenius law, is explained by the Maxwell–Boltzmann distribution of molecular energies (Fig. 18.10). If E_a is the critical relative collision energy required for a pair of molecules to react, only a small fraction of the molecules will have at least this much energy at sufficiently low temperature. This fraction corresponds to the area under the Maxwell–Boltzmann distribution curve between E_a and ∞. As the temperature increases, the distribution function spreads out to include higher energies. The fraction of molecules having more than the critical energy E_a increases exponentially as $\exp(-E_a/RT)$, in agreement with Arrhenius's law and experiment. The reaction rate is then proportional to $\exp(-E_a/RT)$. So, both the strong temperature dependence and the order of magnitude of the experimental rate constants are explained by the kinetic theory of gases.

The Reaction Coordinate and the Activated Complex

Why should there be a critical collision energy E_a for reaction to occur between two molecules? To understand this, let's consider the physical analogy of marbles rolling on a hilly surface. As a marble rolls up a hill, its potential energy increases and its kinetic energy decreases; it slows down as it climbs the hill. If it can reach the top of the hill, it will fall down the other side, whereupon its kinetic energy will increase and its potential energy will decrease. Not every marble will make it over the hill. If its initial speed, and therefore kinetic energy, is too small, a marble will roll only part way up and then fall back down. Only those marbles with initial kinetic energy higher than some critical threshold will pass over the hill.

We can use this physical model to describe molecular collisions and reactions. As two reactant molecules, atoms, or ions approach each other along a **reaction path,** their potential energy increases as the bonds within them distort. At some maximum potential energy the collision partners become connected in an unstable entity called the **activated complex** or **transition state.** The activated complex is the cross-over stage where the smooth ascent in potential energy as the reactants come together becomes a smooth descent as the product molecules separate. As in the case of the marbles, not all pairs of colliding bodies react. Only those pairs with sufficient kinetic energy can stretch bonds and rearrange atoms enough to become the transition state through which reactants become products. If the barrier to reach the transition state is too high, almost all colliding pairs of reactant molecules separate from each other without reacting. The height of the barrier is close to the measured activation energy for the reaction.

Figure 18.11 shows a graph of the potential energy versus position along the reaction path for the reaction

$$\mathrm{NO_2}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{CO_2}(g)$$

Two activation energies are shown in Figure 18.11: $E_{a,f}$ is the activation energy for the forward reaction, and $E_{a,r}$ is that for the reverse reaction, in which NO takes an oxygen atom from CO_2 to form NO_2 and CO. The difference between the two is ΔU, the change in internal energy of the chemical reaction:

$$\Delta U = E_{a,f} - E_{a,r}$$

Whereas ΔU is a thermodynamic quantity that can be obtained from calorimetric measurements, $E_{a,f}$ and $E_{a,r}$ must be found from the temperature dependence of the rate constants for the forward and reverse reactions. In this reaction the forward and reverse activation energies are 132 and 358 kJ mol^{-1}, respectively, and ΔU from thermodynamics is -226 kJ mol^{-1}.

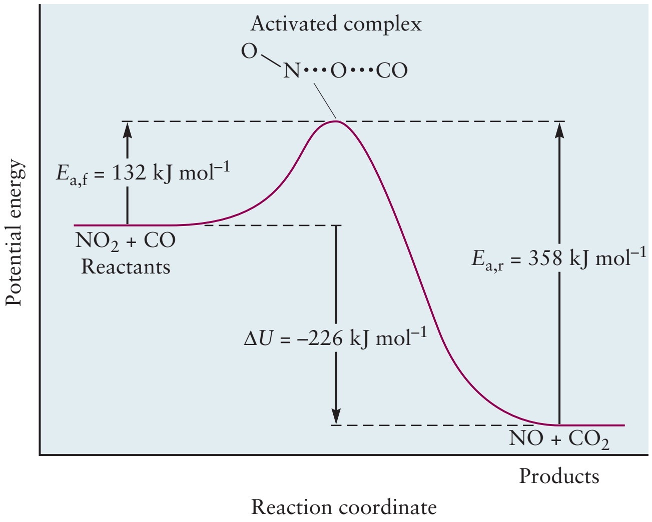


FIGURE 18.11 The energy profile along the reaction coordinate for the reaction $NO_2 + CO \longrightarrow NO + CO_2$. This direct reaction dominates the kinetics at high temperatures (above about 500 K).

The activation energy for an elementary reaction is always positive—although in some cases it can be quite small—because there is always some energy barrier to surmount. Rates of elementary reactions therefore increase with increasing temperature. This is not necessarily true for rates of overall reactions consisting of more than one elementary reaction. These sometimes have "negative activation energies," which means that the overall reaction rate is slower at higher temperature. How can this be? Let's examine a specific example: the reaction of NO with oxygen

$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$$

has the observed rate law

$$\text{rate} = k_{obs}[NO]^2[O_2]$$

where k_{obs} *decreases* with increasing temperature. In Section 18.4 we accounted for this rate expression with a two-step mechanism. The first step is a rapid equilibrium (with equilibrium constant K_1) between two NO molecules and their dimer, N_2O_2. The second step is the slow reaction (with rate constant k_2) of N_2O_2 with O_2 to form products. The overall rate constant is therefore the product of k_2 and K_1. Whereas k_2 is the rate constant for an elementary reaction, and so increases with increasing temperature, K_1 is an *equilibrium* constant and may decrease as temperature increases. Provided the reaction is sufficiently exothermic (as it is in this case), K_1 will decrease so rapidly with increasing temperature that the product k_2K_1 will decrease as well. This combination of effects explains the observation of "negative activation energies" in some overall chemical reactions.

A DEEPER LOOK

18.6 Reaction Dynamics

In this section we first study the dynamics of reactive collisions in the gas phase and connect the predicted results to experimentally measured rate constants. Then we compare these results with the corresponding dynamics for reactions in solution. The starting point is Equation 9.35 from Section 9.8, which gives the rate of collisions of a single molecule with other molecules of the same type:

$$Z_1 = \sqrt{2}\,\pi\,d^2\bar{u}\,\frac{N}{V} = 4\,d^2\sqrt{\frac{\pi RT}{\mathcal{M}}}\,\frac{N}{V}$$

Here d is the molecular diameter, $\bar{u}$ the average speed, $\mathcal{M}$ the molar mass, and N/V the number density of molecules in the gas. If there are N molecules in the volume, the *total* number of collisions per unit time is $\frac{1}{2}N \times Z_1$. (The factor $\frac{1}{2}$ appears because the collision of two A molecules counts as only one collision—not as one collision for the first A molecule with the second, plus another for the second with the first.) The rate of collisions *per unit volume* is then this result divided by V, or

$$\text{rate of collisions per unit volume} = Z_{AA} = 2\,d^2\sqrt{\frac{\pi RT}{\mathcal{M}}}\left(\frac{N}{V}\right)^2$$

The next step is to relate Z_{AA} to the second-order rate constant for the reaction

$$A + A \longrightarrow \text{products}$$

If the activation energy for this reaction is E_a, then only a fraction $\exp(-E_a/RT)$ of these collisions will have sufficient energy to overcome the barrier leading to products. Each such *effective* collision of a pair of A molecules leads to a decrease in the number of A molecules in the reaction mixture by two, so the rate of change of the number of A molecules per unit volume is

$$\frac{d(N/V)}{dt} = -2Z_{AA}e^{-E_a/RT}$$

$$= -2 \times 2\,d^2\sqrt{\frac{\pi RT}{\mathcal{M}}}\,e^{-E_a/RT}\left(\frac{N}{V}\right)^2$$

Rate constants involve the number of *moles* of A per unit volume, [A], not the number of molecules. These two quantities are related by

$$N_A[A] = \frac{N}{V}$$

where N_A is Avogadro's number. Substituting this equation and bringing a factor of $-\frac{1}{2}$ back to the left side (as in our usual definition of reaction rate), we find

$$\text{rate} = -\frac{1}{2}\frac{d[A]}{dt} = 2\,d^2\,N_A\sqrt{\frac{\pi RT}{\mathcal{M}}}\,e^{-E_a/RT}[A]^2$$

The rate constant predicted by simple collision dynamics is thus

$$k = 2\,d^2\,N_A\sqrt{\frac{\pi RT}{\mathcal{M}}}\;e^{-E_a/RT} \qquad [18.7]$$

How well does this simple theory agree with experiment? By fitting data for gas-phase elementary reaction rates to the Arrhenius form, we can obtain the activation energy and the factor A. The value of A can be compared with the theory, once we estimate the molecular diameter. For the elementary reaction

$$2\,\text{NOCl}(g) \longrightarrow 2\,\text{NO}(g) + \text{Cl}_2(g)$$

the measured rate constant is 0.16 times the calculated rate constant. This indicates that not all collisions lead to reaction, even if the molecules have sufficient relative kinetic energy. What other effect have we overlooked? The relative orientations of the colliding molecules certainly should play a role in determining whether a particular collision results in a reaction. In order to split off a Cl_2 molecule as a reaction product, it seems obvious that the two NOCl reactant molecules must approach each other in orientations that bring the chlorine atoms close together (Fig. 18.12). So, the calculated collision frequency must be multiplied by a **steric factor** *P* (0.16 for this reaction) to account for the fact that only a fraction of the collisions occur with the proper orientation to lead to reaction.

We can extend the collision theory to calculate the rate constant for bimolecular reactions of two species, A and B. Comparing observed and predicted rate constants gives the values of *P* shown in Table 18.1. As the colliding molecules become larger and more complex, *P* becomes smaller because a smaller fraction of collisions is effective in causing reaction. The steric factor is an empirical correction that has to be identified by comparing results of the simple theory with experimental data. It can be predicted in more advanced theories but only for especially simple reactions.

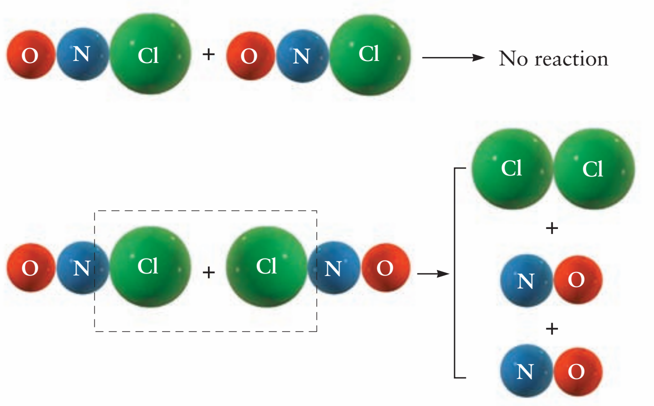


FIGURE 18.12 The steric effect on the probability of a reaction. The two NOCl molecules must approach each other in such a way that the two chlorine atoms are close together, if the encounter is to produce $Cl_2(g)$ and $NO(g)$.

TABLE 18.1 Steric Factors for Gas-Phase Reactions

Reaction	Steric Factor P
$2\,NOCl \longrightarrow 2\,NO + Cl_2$	0.16
$2\,NO_2 \longrightarrow 2\,NO + O_2$	5.0×10^{-2}
$2\,ClO \longrightarrow Cl_2 + O_2$	2.5×10^{-3}
$H_2 + C_2H_4 \longrightarrow C_2H_6$	1.7×10^{-6}

Adapted from P. W. Atkins, *Physical Chemistry,* 5th ed. New York: W. H. Freeman, 1994, p. C30.

Molecular Beams

The kinetics experiments described so far are all carried out by changing reactant concentrations and the temperature. These are macroscopic properties of a reacting mixture, and allow the colliding molecules to have a broad range of energy. So, the results represent averages over range of collision energies. An alternative way to study kinetics and obtain molecular information directly is to use the *crossed molecular beam technique.* In this device two beams of reactant molecules intersect in a chamber under high vacuum, and the reaction products are identified by some appropriate detector (Fig. 18.13).

This apparatus allows the reactant molecules to be prepared in highly selective conditions. A velocity selector between the beam source and the collision region (see Fig. 9.13) will pass only those molecules whose velocities fall within a small range. This permits much finer tuning of reaction energies than can be achieved simply by changing the temperature in a macroscopic kinetics experiment. Electric and magnetic fields or laser light can be applied to select reactant according to how fast they rotate and how much they vibrate. The velocity of products can be measured, their angular distribution relative to the directions of the initial beams can be determined, and their vibration and rotation energies can be determined. All this information allows a much more detailed examination of the way in which molecules collide and react. For example, if the activated complex rotates many times before it finally breaks up into products, the angular distribution of products should be uniform. But if it breaks up before it has a chance to rotate, the angular distribution of products

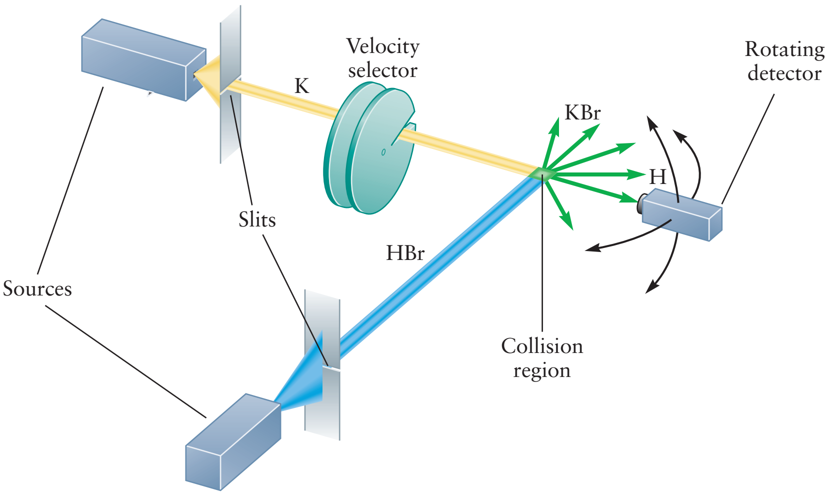


FIGURE 18.13 Diagram of a crossed molecular beam experiment. The reaction being studied is $K + HBr \longrightarrow KBr + H$. The curved arrows on the right side of the figure represent rotation of the detector in the vertical and horizontal planes.

should be very nonuniform and should depend on the directions of the original beams. This type of measurement gives information on the lifetime of an activated complex.

Molecular beams are limited to reactions that are carried out in vacuum, where well-defined beams of reactant molecules can be prepared. This limits their application to gas-phase reactions and to reactions of gaseous molecules with solid surfaces. Molecular beam methods cannot be used to study kinetics in liquid solvents. The detailed information they provide for gas–gas and gas–surface reactions allows precise testing of models and theories for the dynamics of these classes of reactions.

Reaction Kinetics in Liquids

In a gas, atoms or molecules move in straight lines between occasional collisions (see Fig. 9.22). In a liquid the concept of collision has no meaning because molecules interact continuously with not one, but many neighbors. Their trajectories can nonetheless be envisioned as rattling motions of a "test" molecule in a temporary "cage" formed by its neighbors, superimposed on its random and erratic displacement by diffusion. In a time interval *t*, molecules undergo various net displacements Δr. The average of the *square* of their displacements during the interval is found experimentally to be proportional to the time interval:

$$\overline{(\Delta r)^2} = 6\,Dt$$

This is the same law given for gases in Section 9.8, and it applies also to solids (see Section 21.5). The magnitude of the diffusion constant D varies widely from one phase to another. Typical values of D are on the order of 10^{-9} m^2 s^{-1} for liquids (four orders of magnitude smaller than for a typical gas at atmospheric pressure). So in a time interval of 1 s, the mean-square displacement through diffusion is of order 10^{-8} m^2 and the root-mean-square displacement is of order 10^{-4} m (0.1 mm). For larger particles or in more viscous fluids the diffusion coefficient can be much smaller and the resulting displacement smaller as well.

The motion of molecules in a liquid has a significant effect on the kinetics of chemical reactions in solution. Molecules must diffuse together before they can react, so their diffusion constants affect the rate of reaction. If the intrinsic reaction rate of two molecules that come into contact is fast enough (that is, if almost every encounter leads to reaction), then diffusion is the rate-limiting step. Such **diffusion-controlled reactions** have a maximum bimolecular rate constant on the order of 10^{10} L mol^{-1} s^{-1} in aqueous solution for the reaction of two neutral species. If the two species have opposite charges, the reaction rate can be even higher. One of the fastest known reactions in aqueous solution is the neutralization of hydronium ion (H_3O^+) by hydroxide ion (OH^-):

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2\,H_2O(\ell)$$

for which the diffusion-controlled rate constant is greater than 10^{11} L mol^{-1} s^{-1}.

18.7 Kinetics of Catalysis

A **catalyst** is a substance that takes part in a chemical reaction and speeds up the rate but undergoes no permanent chemical change itself. Catalysts therefore do not appear in the overall balanced chemical equation. But their presence very much affects the rate law, modifying and speeding existing pathways or, more commonly, providing completely new pathways by which a reaction can occur (Fig. 18.14). Catalysts have significant effects on reaction rates even when they are present in very small amounts. Industrial chemistry devotes great effort to finding catalysts to accelerate particular desired reactions without increasing the generation of undesired products.

(a) (b)

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FIGURE 18.14 The decomposition of hydrogen peroxide, H_2O_2, to water and oxygen is catalyzed by adding a very small amount of transition metal oxide (a). (b) The water evolves as steam because of the heat given off in the reaction.

Catalysis are classified into two types: homogeneous and heterogeneous. In **homogeneous catalysis** the catalyst is present in the same phase as the reactants, as when a gas-phase catalyst speeds up a gas-phase reaction, or a species dissolved in solution speeds up a reaction in solution. Chlorofluorocarbons and oxides of nitrogen are homogeneous catalysts responsible for the destruction of ozone in the stratosphere. These reactions are examined in more detail in Section 20.5. A second example is the catalysis of the oxidation–reduction reaction

$$\mathrm{Tl}^{+}(aq) + 2\,\mathrm{Ce}^{4+}(aq) \longrightarrow \mathrm{Tl}^{3+}(aq) + 2\,\mathrm{Ce}^{3+}(aq)$$

by silver ions in solution. The direct reaction of Tl^+ with a single Ce^{4+} ion to give Tl^{2+} as an intermediate is slow. The reaction can be speeded up by adding Ag^+ ions, which take part in a reaction mechanism of the form

$$\mathrm{Ag}^{+} + \mathrm{Ce}^{4+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Ag}^{2+} + \mathrm{Ce}^{3+} \qquad \text{(fast)}$$

$$\mathrm{TI}^{+} + \mathrm{Ag}^{2+} \xrightarrow{k_2} \mathrm{TI}^{2+} + \mathrm{Ag}^{+} \qquad \text{(slow)}$$

$$\mathrm{TI}^{2+} + \mathrm{Ce}^{4+} \xrightarrow{k_3} \mathrm{TI}^{3+} + \mathrm{Ce}^{3+} \qquad \text{(fast)}$$

The Ag^+ ions are not permanently transformed by this reaction because those used up in the first step are regenerated in the second; they play the role of catalyst in significantly speeding the rate of the overall reaction.

In **heterogeneous catalysis** the catalyst is present as a phase distinct from the reaction mixture. The most important case is the catalytic action of certain solid surfaces on gas-phase and solution-phase reactions. A critical step in the production of sulfuric acid relies on a solid oxide of vanadium (V_2O_5) as catalyst. Many other solid catalysts are used in industrial processes. One of the best studied is the addition of hydrogen to ethylene to form ethane:

$$\mathrm{C_2H_4}(g) + \mathrm{H_2}(g) \longrightarrow \mathrm{C_2H_6}(g)$$

The process occurs extremely slowly in the gas phase but is catalyzed by a platinum surface (Fig. 18.15).

Another example is the solid catalyst used to reduce the emission of pollutants such as unburned hydrocarbons, carbon monoxide, and nitrogen oxides in the exhaust streams of automobile engines (Fig. 18.16). A **catalytic converter** is designed to simultaneously *oxidize* hydrocarbons and CO through the reactions

$$\mathrm{CO},\ \mathrm{C}_x\mathrm{H}_y,\ \mathrm{O_2} \xrightarrow{\text{Catalyst}} \mathrm{CO_2},\ \mathrm{H_2O}$$

and *reduce* nitrogen oxides through the reactions

$$\mathrm{NO},\ \mathrm{NO_2} \xrightarrow{\text{Catalyst}} \mathrm{N_2},\ \mathrm{O_2}$$

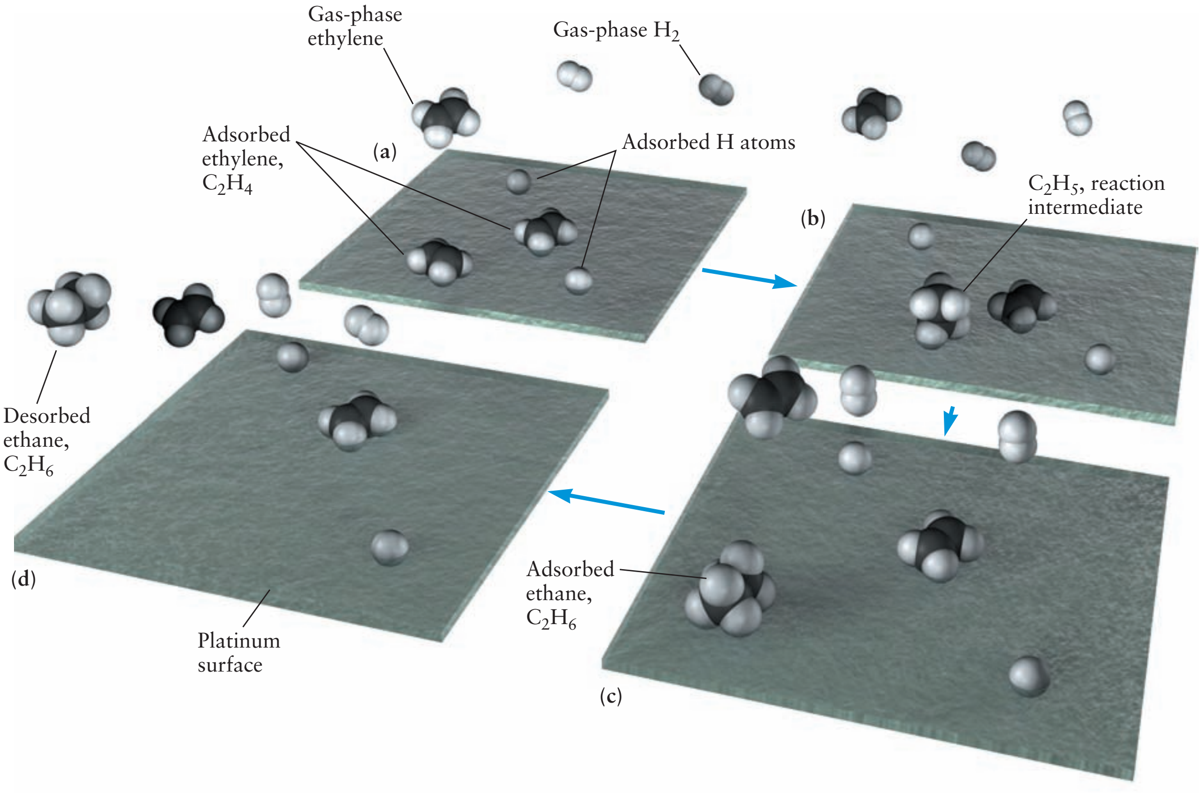

FIGURE 18.15 Platinum catalyzes the reaction $H_2 + C_2H_4$ by providing a surface that promotes the dissociation of H_2 to H atoms, which can then add to the C_2H_4 stepwise to give ethane, C_2H_6.

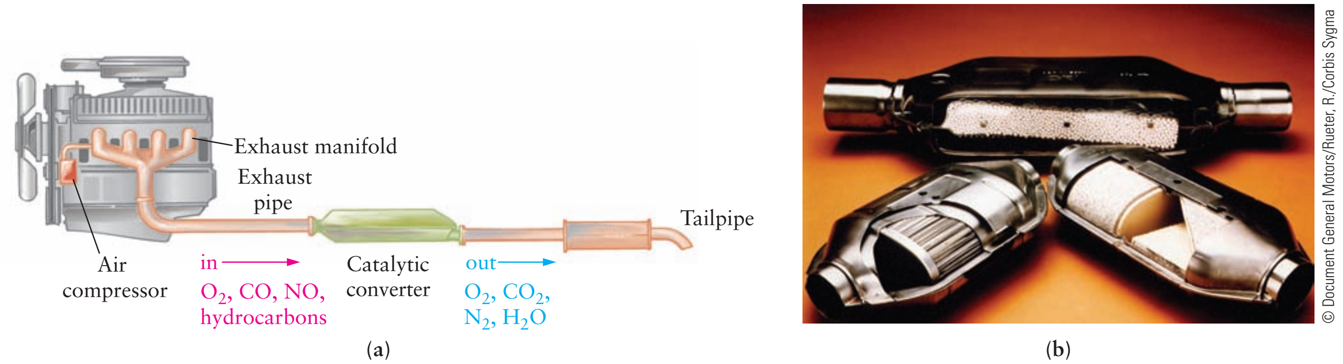

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FIGURE 18.16 (a) The arrangement of a catalytic converter used to reduce automobile pollution. (b) Cutaway views of several catalytic converters showing different structures for organizing metal catalysts, platinum, palladium, and rhodium on different substrates and supports. A steel-alloy heating element raises the temperature to 400°C in seconds, activating the catalysts and reducing the pollution emitted in the first minutes after the car is started.

Clearly, the best catalyst for the reduction reactions may not be the best for the oxidation reactions, so two catalysts are combined. The noble metals, although expensive, are particularly useful. Typically, platinum and rhodium are deposited on a fine honeycomb mesh of alumina (Al_2O_3) to give a large surface area that increases the contact time of the exhaust gas with the catalysts. The platinum serves primarily as an oxidation catalyst and the rhodium as a reduction catalyst. Catalytic converters can be poisoned with certain metals that block their active sites and reduce their effectiveness. Because lead is one of the most serious such poisons, automobiles with catalytic converters must use unleaded fuel.

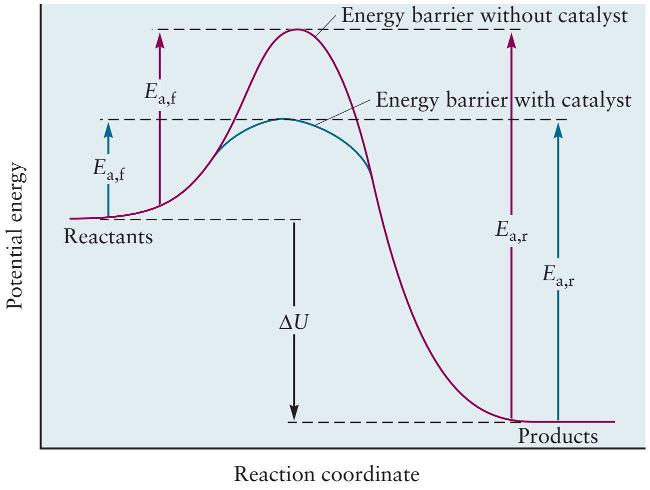


FIGURE 18.17 The most important way in which catalysts speed reactions is by reducing the activation energy. Both the uncatalyzed (blue) and catalyzed (red) reaction coordinates are shown.

A catalyst speeds up the rate of a reaction by increasing the Arrhenius factor A. More often a catalyst lowers the activation energy E_a by providing a new reaction pathway through a different activated complex with lower potential energy (Fig. 18.17). A corollary of this fact is that the same catalyst will speed both the forward *and* reverse reactions, because it lowers both the forward and reverse activation energies equally. It is important to remember that a catalyst does not change the thermodynamics of the overall reaction. Because the free energy is a function of state, ΔG is independent of the path followed and therefore the equilibrium constant is not changed by a catalyst. Reaction products not favored by thermodynamics still do not form. The role of catalysts is to speed up the rate of production of products that *are* allowed by thermodynamics.

An **inhibitor** plays an opposite role to a catalyst. It slows the rate of a reaction, often by increasing the activation energy. Like catalysts, inhibitors are important in the chemical industries because they reduce the rates of undesirable side reactions, allowing desired products to form in greater yield.

Enzyme Catalysis

Many chemical reactions in living systems are catalyzed by enzymes. An **enzyme** is a large protein molecule (typically of molar mass 20,000 g mol^{-1} or more) with a structure capable of carrying out a specific reaction or series of reactions. One or more reactant molecules (called **substrates**) bind to an enzyme at its **active sites.** These are regions on the surface of the enzyme where the local structures and chemical properties will selectively bind a specific substrate so particular chemical transformations of it can be carried out (Fig. 18.18). Many enzymes are quite specific in their active sites. The enzyme urease catalyzes the hydrolysis of urea, $(NH_2)_2CO$,

$$H_3O^+(aq) + (NH_2)_2CO(aq) + H_2O(\ell) \xrightarrow{\text{Urease}} 2\ NH_4^+(aq) + HCO_3^-(aq)$$

but will not bind most other kinds of molecules, even those of similar structure. In some cases a second species *does* bind to the enzyme and acts as an inhibitor, preventing the enzyme from its usual role as catalyst.

We summarize the kinetics of enzyme catalysis schematically by the reaction mechanism

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES$$

$$ES \xrightarrow{k_2} E + P$$

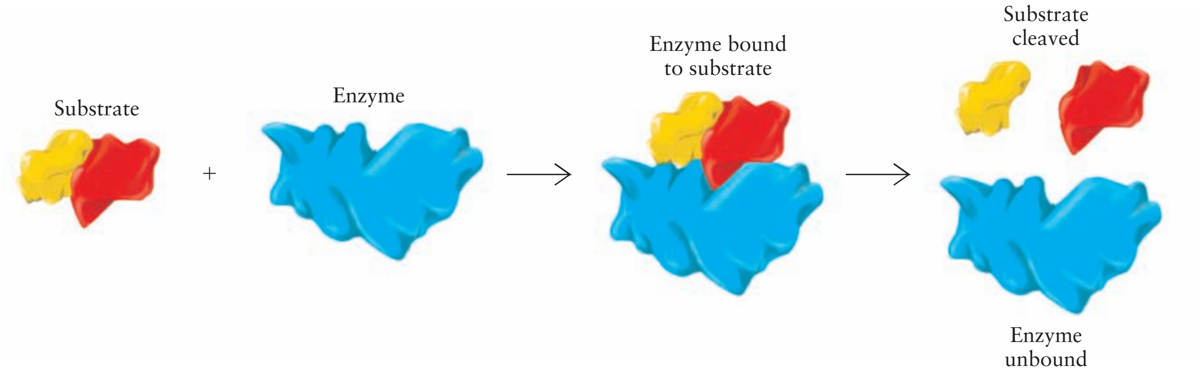


FIGURE 18.18 The binding of a substrate to an enzyme and the subsequent reaction of the substrate. As this schematic figure suggests, the size and shape of the active site play a role in determining which substrates bind. Equally important are the strengths of the intermolecular forces between nearby groups on the enzyme and substrate.

Here E stands for the free enzyme, S for the substrate, ES for the complex formed when the substrate binds to the active site, and P for the product of the chemical transformation. We can obtain the rate of formation of P through this mechanism from the steady-state approximation for the concentration of the enzyme-substrate complex, [ES]. As Section 18.4 shows, this approximation involves setting the rate of change of [ES] to 0:

$$\frac{d[\mathrm{ES}]}{dt} = 0 = k_1[\mathrm{E}][\mathrm{S}] - k_{-1}[\mathrm{ES}] - k_2[\mathrm{ES}]$$

This equation could be solved to find [ES] in terms of [E], but that is not quite what we want. Here [E] is the concentration of free enzyme which does not have substrate bound to it, and [ES] is the concentration of bound enzyme. Their sum is $[\mathrm{E}]_0$, the total amount of enzyme present:

$$[\mathrm{E}]_0 = [\mathrm{E}] + [\mathrm{ES}]$$

Because $[\mathrm{E}]_0$ is the quantity accessible to experiment, we replace [E] in the preceding steady-state equation with $[\mathrm{E}]_0 - [\mathrm{ES}]$. This gives

$$\frac{d[\mathrm{ES}]}{dt} = 0 = k_1[\mathrm{E}]_0[\mathrm{S}] - k_1[\mathrm{ES}][\mathrm{S}] - k_{-1}[\mathrm{ES}] - k_2[\mathrm{ES}]$$

which can be solved for [ES] to give

$$[\mathrm{ES}] = \frac{k_1[\mathrm{E}]_0[\mathrm{S}]}{k_1[\mathrm{S}] + (k_{-1} + k_2)}$$

If K_m is defined by

$$K_\mathrm{m} = \frac{k_{-1} + k_2}{k_1}$$

then

$$[\mathrm{ES}] = \frac{[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + K_\mathrm{m}}$$

The rate of formation of product is

$$\boxed{\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}] = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + K_\mathrm{m}}} \qquad [18.8]$$

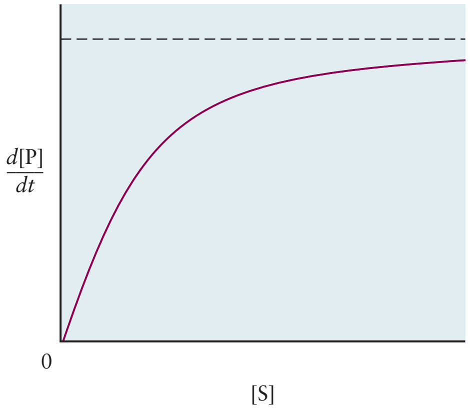


FIGURE 18.19 The dependence of the rate of an enzyme reaction on substrate concentration. The dashed line gives the rate attained for very high [S].

This is the **Michaelis–Menten equation,** which describes the kinetics of many enzyme-catalyzed reactions. Figure 18.19 shows a typical experimental curve for the dependence of the rate of such a reaction on substrate concentration [S]. For low substrate concentrations the rate is linear in [S], but at high concentrations it levels off. This behavior is easily understood on physical grounds. When [S] is small, the more substrate is added, the greater is the rate of formation of product. As the amount of substrate becomes large, all the active sites of the enzyme molecules are bound to substrate, so adding more S does not affect the rate of the reaction. Saturation occurs, and the rate levels off.

By taking the inverse of each side of the Michaelis–Menten equation, we obtain the very useful alternative form

$$\frac{1}{d[\mathrm{P}]/dt} = \frac{1}{k_2[\mathrm{E}]_0} + \frac{K_{\mathrm{m}}}{k_2[\mathrm{E}]_0[\mathrm{S}]}$$

Using this form of the Michaelis–Menten equation, we see that plotting the inverse of the reaction rate against the inverse of the substrate concentration should produce a straight line whose slope and intercept are $k_2[\mathrm{E}]_0$ and K_{m}, respectively.

CHAPTER SUMMARY

Chemical kinetics is the study of the rates of chemical reactions and the factors that control those rates. The rates of chemical reactions depend on the concentrations of all of the reactants and products as well as the temperature. The concentration dependence of reaction rates is given by empirical rate laws in which the rate depends on the concentration of each reactant raised to some power that is not, in general, related to the stoichiometric coefficients in the balanced equation for the reaction. Rate laws may be determined by measuring the initial rate of a reaction as a function of initial concentration or by inspecting the concentration-time profile over the course of the reaction. Concentrations decrease exponentially with time for first order reactions and the half-life is a characteristic time scale for the reaction. Most chemical reactions occur as a series of elementary reactions, which constitute the reaction mechanism. The steady state approximation provides a simple framework to analyze the kinetics of multistep reactions. This approximation, which is widely used in many areas of chemistry and biochemistry, shows how a reaction may display either first or second order kinetics, depending on starting concentrations. It also accounts for the rate-limiting step, which determines the overall rate of the reaction. Spectroscopic detection or chemical trapping of reaction intermediates is a powerful way to establish a reaction mechanism. The rates of all elementary reactions increase with increasing temperature. As temperatures rise, more molecules have enough energy to overcome the activation barrier and proceed to form products. Chemical kinetics is a fascinating subject covering time scales that range from femtoseconds (primary photochemical processes) to eons (geochemical and astrochemical processes). The fundamental principles developed in this chapter can be applied to understand the rates and mechanism of chemical reactions in these very different areas of science.

CUMULATIVE EXERCISE

Sulfite and Sulfate Kinetics

Sulfur dioxide dissolves in water droplets (fog, clouds, and rain) in the atmosphere and reacts according to the equation

$$SO_2(aq) + 2\,H_2O(\ell) \longrightarrow HSO_3^-(aq) + H_3O^+(aq)$$

$HSO_3^-(aq)$ (hydrogen sulfite ion) is then slowly oxidized by oxygen that is also dissolved in the droplets:

$$2\,HSO_3^-(aq) + O_2(aq) + 2\,H_2O(\ell) \longrightarrow 2\,SO_4^{2-}(aq) + 2\,H_3O^+(aq)$$

Although the second reaction has been studied for many years, only recently was it shown to proceed by the steps

$$2\,HSO_3^-(aq) + O_2(aq) \longrightarrow S_2O_7^{2-}(aq) + H_2O(\ell) \qquad \text{(fast)}$$

$$S_2O_7^{2-}(aq) + 3\,H_2O(\ell) \longrightarrow 2\,SO_4^{2-}(aq) + 2\,H_3O^+(aq) \qquad \text{(slow)}$$

The reactive intermediate, $S_2O_7^{2-}(aq)$, which had not been detected in earlier studies of this reaction, is well known in other reactions. It is the *disulfate* ion.

In an experiment at 25°C, a solution was mixed with the realistic initial concentrations of 0.270 M $HSO_3^-(aq)$ and 0.0135 M $O_2(aq)$. The initial pH was 3.90. The following table tells what happened in the solution, beginning at the moment of mixing.

Time(s)	$[HSO_3^-]$ (M)	$[O_2]$ (M)	$[S_2O_7^{2-}]$ (M)	$[HSO_4^-] + [SO_4^{2-}]$ (M)
0.000	0.270	0.0135	0.000	0.000
0.010	0.243	0.000	13.5×10^{-3}	0.000
10.0	0.243	0.000	11.8×10^{-3}	03.40×10^{-3}
45.0	0.243	0.000	7.42×10^{-3}	12.2×10^{-3}
90.0	0.243	0.000	4.08×10^{-3}	18.8×10^{-3}
150.0	0.243	0.000	1.84×10^{-3}	23.3×10^{-3}
450.0	0.243	0.000	0.034×10^{-3}	26.9×10^{-3}
600.0	0.243	0.000	0.005×10^{-3}	27.0×10^{-3}

(a) Determine the average rate of increase of the total of the concentrations of the sulfate plus hydrogen sulfate ions during the first 10 s of the experiment.

(b) Determine the average rate of disappearance of hydrogen sulfite ion during the first 0.010 s of the experiment.

(c) Explain why the hydrogen sulfite ion stops disappearing after 0.010 s.

(d) Plot the concentration of disulfate ion versus time on graph paper, and use the graph to estimate the instantaneous rate of disappearance of disulfate ion 90.0 s after the reaction starts.

(e) Determine the order with respect to the disulfate ion of the second step of the conversion, and the rate constant of that step.

(f) Determine the half-life of the second step of the conversion process.

(g) At 15°C the rate constant of the second step of the conversion is only 62% of its value at 25°C. Compute the activation energy of the second step.

(h) The first step of the conversion occurs much faster when 1.0×10^{-6} M $Fe^{2+}(aq)$ ion is added (but the rate of the second step is unaffected). What role does Fe^{2+} play?

(i) Write a balanced equation for the overall reaction that gives sulfuric acid from SO_2 dissolved in water droplets in the air.

Answers

(a) 3.40×10^{-4} mol L^{-1} s^{-1}

(b) 2.7 mol L^{-1} s^{-1}

(c) All of the oxygen is consumed, so the first step of the process is over.

(d) 5.43×10^{-5} mol L^{-1} s^{-1}

(e) First order; $k = 0.0133$ s^{-1}

(f) 52 s

(g) 34 kJ mol^{-1}

(h) Fe^{2+} acts as a catalyst.

(i) $2\ SO_2(aq) + O_2(aq) + 6\ H_2O(\ell) \longrightarrow SO_4^{2-}(aq) + 4\ H_3O^+(aq)$

CHAPTER REVIEW

- The average rate of a chemical reaction is the change in concentration of one of the reactants or products over a finite interval of time. The instantaneous rate is the slope of a plot of concentration versus time at a particular point in time. The rate of the reaction is given by the rate for a particular species divided by its stoichiometric coefficient.
- The rates of all chemical reactions depend on the concentrations of reactants. This concentration dependence is expressed in the empirical rate law in which the rate is proportional to the concentration of reactants raised to some power. The power is not necessarily related to the stoichiometric coefficient in the balanced reaction.
- The order of the reaction with respect to each species is the power to which the concentration of that species is raised in the empirical rate law. The overall order of the reaction is the sum of the individual reaction orders.
- Integrated rate laws show how the concentration of a particular species changes over time, and they can be useful in deducing empirical rate laws and rate constants when it is difficult to measure initial rates.
- $c(t) = c_0 e^{-kt}$ for a first order reaction.

  A plot of $\ln [c(t)]$ versus t is a straight line with slope $-k$.

  The half-life, $t_{1/2}$, is the time it takes for the concentration to decrease to half its initial value.

  $t_{1/2}$ is independent of concentration for first order reactions and it provides a convenient way to characterize the rates of first order reactions.
- $\frac{1}{c} = \frac{1}{c_0} + 2kt$ for second order reactions written in the form $2A \longrightarrow$ products.

  A plot of $1/c$ versus t is a straight line with slope $2k$.

  The half life in second order reactions is not independent of time and is not a very useful measure of the reaction rate.
- A reaction mechanism is the detailed sequence of elementary reactions that lead to the overall chemical reaction.

  An elementary reaction occurs exactly as its balanced equation implies.

  - Dissociation of a reactant in the absence of any other reactants is a unimolecular elementary reaction.
  - Bimolecular elementary reactions are the most common in chemistry; they result from single bimolecular collisions between two reactants.
  - Termolecular reactions resulting from simultaneous collisions of three reactants are rare.
- The principle of detailed balance connects kinetics and chemical equilibrium. The rates of forward and reverse reactions for elementary reactions must be the same at equilibrium so $\frac{k_f}{k_r} = K$.
- Writing empirical rate laws for reactions whose mechanisms have been established is straightforward; inferring mechanisms from empirical rate laws is not. Direct detection or trapping of reactive intermediates provides the strongest evidence in support of a proposed mechanism.
- One elementary reaction is often slower than all the others in a multi-step mechanism. The rate of the overall reaction is limited by this rate-determining step. Elementary reactions that precede the rate-limiting step are often at equilibrium.
- The steady-state approximation provides a simple framework for analyzing the kinetics of many chemical reactions.
  - The mechanism is a sequence of two reactions; the first step is reversible and the second step is irreversible.
  - At low pressures or concentrations the first step is rate limiting and second order kinetics are observed.
  - At high pressures or concentrations equilibrium is established in the first step and the second step is rate limiting. First order kinetics are observed.
- Chain reactions proceed through a series of elementary reactions, one or more of which is repeated many times.
  - Reactive intermediates are generated at initiation.
  - Products are formed by propagation (with intermediate concentrations at steady state).
  - The reaction terminates when two reactive intermediates combine to form a stable product.
- The rates of all elementary reactions increase with increasing temperatures.
  - Collision rates increase with increasing temperature.
  - The number of effective collisions increases dramatically because the fraction of molecules (calculated using the Boltzmann distribution) with energy greater than the activation energy is greater.
  - The empirical Arrhenius equation, $k = Ae^{-E_A/RT}$, accounts for the increase in the number of effective collisions in the exponential term, whereas the pre-exponential factor, A, is assumed to be temperature independent.
- The activated complex or transition state is the configuration of the system with the highest potential energy. The energy difference between the reactants and the transition state is the activation energy for the reaction. Only those molecules with enough energy to surmount the barrier will react.
- Reaction dynamics provide a microscopic picture of chemical reactions that connect to the macroscopic kinetics.
  - Rates of bimolecular collisions are calculated using the kinetic theory of gases to arrive at the Arrhenius pre-exponential factor and the activation energy is measured experimentally.
  - Observed rates can be factors of 10^{-6} smaller than those predicted from simple reaction dynamics suggesting that a steric factor, which accounts for the relative orientations of the reactants, is extremely important in determining reaction rates.

- Catalysts increase the rates of chemical reactions by providing alternate paths that have lower activation barriers.
  - The transition state in the catalyzed reaction is generally different than in the uncatalyzed reaction.
  - Homogeneous catalysts are present in the same phase as the reaction being catalyzed whereas heterogeneous catalysts are present in a different phase.
- Enzymes are biological catalysts that bind substrates with exquisite selectivity, position reactants at optimal locations and stabilize transition states, all of which leads to lower activation barriers than those in the uncatalyzed reaction.

CONCEPTS & SKILLS

After studying this chapter and working the problems that follow, you should be able to:

1. Describe experimental methods for measuring average and instantaneous rates (Section 18.1, Problems 1–2).
2. Deduce rate laws and reaction orders from experimental measurements of the dependence of reaction rates on concentrations (Section 18.2, Problems 5–8).
3. Use the integrated rate laws for first- and second-order reactions to calculate the concentrations remaining after a certain elapsed time (Section 18.2, Problems 9–18).
4. Describe the relationship between the equilibrium constant for a reaction and the corresponding forward and reverse rate constants (Section 18.3, Problems 23–24).
5. Deduce the rate law from a mechanism characterized by a single rate-determining step (Section 18.4, Problems 25–30).
6. Use the steady-state approximation to deduce rate laws when no single rate-determining step exists (Section 18.4, Problems 31–34).
7. Calculate Arrhenius factors and activation energies from measurements of the temperature dependence of rate constants (Section 18.5, Problems 35–40).
8. Discuss the connection between activation energy and the energy distribution of molecules, and relate the forward and reverse activation energies to each other through thermodynamics (Section 18.5, Problems 41–42).
9. Outline the quantitative calculation of rate constants, using the collision theory of gases (Section 18.6, Problems 43–44).
10. Describe several types of catalysts and their effects on chemical reactions (Section 18.7).
11. Relate the rate of an enzyme-catalyzed reaction to the concentrations of substrate and enzyme in the reaction mixture (Section 18.7, Problems 45–46).

KEY EQUATIONS

$$\text{rate} = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = -\frac{1}{b}\frac{d[\mathrm{B}]}{dt} = \frac{1}{c}\frac{d[\mathrm{C}]}{dt} = \frac{1}{d}\frac{d[\mathrm{D}]}{dt}$$ **(Section 18.1)**

$$c = c_0\, e^{-kt}$$ **(Section 18.2)**

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k}$$ **(Section 18.2)**

$$\frac{1}{c} = \frac{1}{c_0} + 2kt \qquad \text{(Section 18.2)}$$

$$k = Ae^{-E_a/RT} \qquad \text{(Section 18.5)}$$

$$\ln k = \ln A - \frac{E_a}{RT} \qquad \text{(Section 18.5)}$$

$$k = 2\, d^2\, N_A \sqrt{\frac{\pi RT}{\mathcal{M}}}\, e^{-E_a/RT} \qquad \text{(Section 18.6)}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}] = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + K_m} \qquad \text{(Section 18.7)}$$

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G. Problems that are more challenging are indicated with asterisks.

Rates of Chemical Reactions

1. Use Figure 18.3 to estimate graphically the instantaneous rate of production of NO at $t = 200$ s.

2. Use Figure 18.3 to estimate graphically the instantaneous rate of production of NO at $t = 100$ s.

3. Give three related expressions for the rate of the reaction

$$N_2(g) + 3\ H_2(g) \longrightarrow 2\ NH_3(g)$$

assuming that the concentrations of any intermediates are constant and that the volume of the reaction vessel does not change.

4. Give four related expressions for the rate of the reaction

$$2\ H_2CO(g) + O_2(g) \longrightarrow 2\ CO(g) + 2\ H_2O(g)$$

assuming that the concentrations of any intermediates are constant and that the volume of the reaction vessel does not change.

Rate Laws

5. Nitrogen oxide reacts with hydrogen at elevated temperatures according to the following chemical equation:

$$2\ NO(g) + 2\ H_2(g) \longrightarrow N_2(g) + 2\ H_2O(g)$$

It is observed that, when the concentration of H_2 is cut in half, the rate of the reaction is also cut in half. When the concentration of NO is multiplied by 10, the rate of the reaction increases by a factor of 100.

(a) Write the rate expression for this reaction, and give the units of the rate constant k.

(b) If [NO] were multiplied by 3 and $[H_2]$ by 2, what change in the rate would be observed?

6. In the presence of vanadium oxide, $SO_2(g)$ reacts with an excess of oxygen to give $SO_3(g)$:

$$SO_2(g) + \tfrac{1}{2}\ O_2(g) \xrightarrow{V_2O_5} SO_3(g)$$

This reaction is an important step in the manufacture of sulfuric acid. It is observed that tripling the SO_2 concentration increases the rate by a factor of 3, but tripling the SO_3 concentration decreases the rate by a factor of $1.7 \approx \sqrt{3}$. The rate is insensitive to the O_2 concentration as long as an excess of oxygen is present.

(a) Write the rate expression for this reaction, and give the units of the rate constant k.

(b) If $[SO_2]$ is multiplied by 2 and $[SO_3]$ by 4 but all other conditions are unchanged, what change in the rate will be observed?

7. In a study of the reaction of pyridine (C_5H_5N) with methyl iodide (CH_3I) in a benzene solution, the following set of initial reaction rates was measured at 25°C for different initial concentrations of the two reactants:

$[C_5H_5N]$ (mol L^{-1})	$[CH_3I]$ (mol L^{-1})	Rate (mol L^{-1} s^{-1})
1.00×10^{-4}	1.00×10^{-4}	7.5×10^{-7}
2.00×10^{-4}	2.00×10^{-4}	3.0×10^{-6}
2.00×10^{-4}	4.00×10^{-4}	6.0×10^{-6}

(a) Write the rate expression for this reaction.

(b) Calculate the rate constant k, and give its units.

(c) Predict the initial reaction rate for a solution in which $[C_5H_5N]$ is 5.0×10^{-5} M and $[CH_3I]$ is 2.0×10^{-5} M.

8. The rate for the oxidation of iron(II) by cerium(IV)

$$Ce^{4+}(aq) + Fe^{2+}(aq) \longrightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$$

is measured at several different initial concentrations of the two reactants:

$[Ce^{4+}]$ (mol L^{-1})	$[Fe^{2+}]$ (mol L^{-1})	Rate (mol L^{-1} s^{-1})
1.1×10^{-5}	1.8×10^{-5}	2.0×10^{-7}
1.1×10^{-5}	2.8×10^{-5}	3.1×10^{-7}
3.4×10^{-5}	2.8×10^{-5}	9.5×10^{-7}

(a) Write the rate expression for this reaction.

(b) Calculate the rate constant k, and give its units.

(c) Predict the initial reaction rate for a solution in which $[Ce^{4+}]$ is 2.6×10^{-5} M and $[Fe^{2+}]$ is 1.3×10^{-5} M.

9. The reaction $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$ is first order, with a rate constant of $2.2 \times 10^{-5}\ s^{-1}$ at 320°C. The partial pressure of $SO_2Cl_2(g)$ in a sealed vessel at 320°C is 1.0 atm. How long will it take for the partial pressure of $SO_2Cl_2(g)$ to fall to 0.50 atm?

10. The reaction $FClO_2(g) \longrightarrow FClO(g) + O(g)$ is first order with a rate constant of $6.76 \times 10^{-4}\ s^{-1}$ at 322°C.
(a) Calculate the half-life of the reaction at 322°C.
(b) If the initial partial pressure of $FClO_2$ in a container at 322°C is 0.040 atm, how long will it take to fall to 0.010 atm?

11. The decomposition of benzene diazonium chloride

$$C_6H_5N_2Cl \longrightarrow C_6H_5Cl + N_2$$

follows first-order kinetics with a rate constant of $4.3 \times 10^{-5}\ s^{-1}$ at 20°C. If the initial partial pressure of $C_6H_5N_2Cl$ is 0.0088 atm, calculate its partial pressure after 10.0 hours.

12. At 600 K, the rate constant for the first-order decomposition of nitroethane

$$CH_3CH_2NO_2(g) \longrightarrow C_2H_4(g) + HNO_2(g)$$

is $1.9 \times 10^{-4}\ s^{-1}$. A sample of $CH_3CH_2NO_2$ is heated to 600 K, at which point its initial partial pressure is measured to be 0.078 atm. Calculate its partial pressure after 3.0 hours.

13. Chloroethane decomposes at elevated temperatures according to the reaction

$$C_2H_5Cl(g) \longrightarrow C_2H_4(g) + HCl(g)$$

This reaction obeys first-order kinetics. After 340 s at 800 K, a measurement shows that the concentration of C_2H_5Cl has decreased from 0.0098 mol L^{-1} to 0.0016 mol L^{-1}. Calculate the rate constant k at 800 K.

14. The isomerization reaction

$$CH_3NC \longrightarrow CH_3CN$$

obeys the first-order rate law

$$\text{rate} = -k[CH_3NC]$$

in the presence of an excess of argon. Measurements at 500 K reveal that in 520 s the concentration of CH_3NC decreases to 71% of its original value. Calculate the rate constant k of the reaction at 500 K.

15. At 25°C in CCl_4 solvent, the reaction

$$I + I \longrightarrow I_2$$

is second order in the concentration of the iodine atoms. The rate constant k has been measured as 8.2×10^9 L mol^{-1} s^{-1}. Suppose the initial concentration of I atoms is 1.00×10^{-4} M. Calculate their concentration after 2.0×10^{-6} s.

16. HO_2 is a highly reactive chemical species that plays a role in atmospheric chemistry. The rate of the gas-phase reaction

$$HO_2(g) + HO_2(g) \longrightarrow H_2O_2(g) + O_2(g)$$

is second order in $[HO_2]$, with a rate constant at 25°C of 1.4×10^9 L mol^{-1} s^{-1}. Suppose some HO_2 with an initial concentration of 2.0×10^{-8} M could be confined at 25°C. Calculate the concentration that would remain after 1.0 s, assuming no other reactions take place.

17. The rate for the reaction

$$OH^-(aq) + NH_4^+(aq) \longrightarrow H_2O(\ell) + NH_3(aq)$$

is first order in both OH^- and NH_4^+ concentrations, and the rate constant k at 20°C is 3.4×10^{10} L mol^{-1} s^{-1}. Suppose 1.00 L of a 0.0010 M NaOH solution is rapidly mixed with the same volume of 0.0010 M NH_4Cl solution. Calculate the time (in seconds) required for the OH^- concentration to decrease to a value of 1.0×10^{-5} M.

18. The rate for the reaction

$$OH^-(aq) + HCN(aq) \longrightarrow H_2O(\ell) + CN^-(aq)$$

is first order in both OH^- and HCN concentrations, and the rate constant k at 25°C is 3.7×10^9 L mol^{-1} s^{-1}. Suppose 0.500 L of a 0.0020 M NaOH solution is rapidly mixed with the same volume of a 0.0020 M HCN solution. Calculate the time (in seconds) required for the OH^- concentration to decrease to a value of 1.0×10^{-4} M.

Reaction Mechanisms

19. Identify each of the following elementary reactions as unimolecular, bimolecular, or termolecular, and write the rate expression.
(a) $HCO + O_2 \longrightarrow HO_2 + CO$
(b) $CH_3 + O_2 + N_2 \longrightarrow CH_3O_2 + N_2$
(c) $HO_2NO_2 \longrightarrow HO_2 + NO_2$

20. Identify each of the following elementary reactions as unimolecular, bimolecular, or termolecular, and write the rate expression.
(a) $BrONO_2 \longrightarrow BrO + NO_2$
(b) $HO + NO_2 + Ar \longrightarrow HNO_3 + Ar$
(c) $O + H_2S \longrightarrow HO + HS$

21. Consider the following reaction mechanism:

$$H_2O_2 \longrightarrow H_2O + O$$
$$O + CF_2Cl_2 \longrightarrow ClO + CF_2Cl$$
$$ClO + O_3 \longrightarrow Cl + 2\,O_2$$
$$Cl + CF_2Cl \longrightarrow CF_2Cl_2$$

(a) What is the molecularity of each elementary step?
(b) Write the overall equation for the reaction.
(c) Identify the reaction intermediate(s).

22. Consider the following reaction mechanism:

$$NO_2Cl \longrightarrow NO_2 + Cl$$
$$Cl + H_2O \longrightarrow HCl + OH$$
$$OH + NO_2 + N_2 \longrightarrow HNO_3 + N_2$$

(a) What is the molecularity of each elementary step?
(b) Write the overall equation for the reaction.
(c) Identify the reaction intermediate(s).

23. The rate constant of the elementary reaction

$$BrO(g) + NO(g) \longrightarrow Br(g) + NO_2(g)$$

is 1.3×10^{10} L mol^{-1} s^{-1} at 25°C, and its equilibrium constant is 5.0×10^{10} at this temperature. Calculate the rate constant at 25°C of the elementary reaction

$$Br(g) + NO_2(g) \longrightarrow BrO(g) + NO(g)$$

24. The compound $IrH_3(CO)(P(C_6H_5)_3)_2$ exists in two forms: the meridional ("mer") and facial ("fac"). At 25°C in a nonaqueous solvent, the reaction mer ⟶ fac has a rate constant of 2.33 s^{-1}, and the reaction fac ⟶ mer has a rate constant of 2.10 s^{-1}. What is the equilibrium constant of the mer-to-fac reaction at 25°C?

Reaction Mechanisms and Rate

25. Write the overall reaction and rate laws that correspond to the following reaction mechanisms. Be sure to eliminate intermediates from the answers.

(a) $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$ (fast equilibrium)
$C + E \xrightarrow{k_2} F$ (slow)

(b) $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + C$ (fast equilibrium)
$C + D \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E$ (fast equilibrium)
$E \xrightarrow{k_3} F$ (slow)

26. Write the overall reaction and the rate laws that correspond to the following reaction mechanisms. Be sure to eliminate intermediates from the answers.

(a) $2\ A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} D$ (fast equilibrium)
$D + B \xrightarrow{k_2} E + F$ (slow)
$F \xrightarrow{k_3} G$ (fast)

(b) $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$ (fast equilibrium)
$C + D \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} F$ (fast equilibrium)
$F \xrightarrow{k_3} G$ (slow)

27. HCl reacts with propene (CH_3CHCH_2) in the gas phase according to the overall reaction

$$HCl + CH_3CHCH_2 \longrightarrow CH_3CHClCH_3$$

The experimental rate expression is

$$\text{rate} = k[HCl]^3[CH_3CHCH_2]$$

Which, if any, of the following mechanisms are consistent with the observed rate expression?

(a) $HCl + HCl \rightleftharpoons H + HCl_2$ (fast equilibrium)
$H + CH_3CHCH_2 \longrightarrow CH_3CHCH_3$ (slow)
$HCl_2 + CH_3CHCH_3 \longrightarrow CH_3CHClCH_3 + HCl$ (fast)

(b) $HCl + HCl \rightleftharpoons H_2Cl_2$ (fast equilibrium)
$HCl + CH_3CHCH_2 \rightleftharpoons CH_3CHClCH_3^*$ (fast equilibrium)
$CH_3CHClCH_3^* + H_2Cl_2 \longrightarrow CH_3CHClCH_3 + 2\ HCl$ (slow)

(c) $HCl + CH_3CHCH_2 \rightleftharpoons H + CH_3CHClCH_2$ (fast equilibrium)
$H + HCl \rightleftharpoons H_2Cl$ (fast equilibrium)
$H_2Cl + CH_3CHClCH_2 \longrightarrow HCl + CH_3CHClCH_3$ (slow)

28. Chlorine reacts with hydrogen sulfide in aqueous solution

$$Cl_2(aq) + H_2S(aq) \longrightarrow S(s) + 2\ H^+(aq) + 2\ Cl^-(aq)$$

in a second-order reaction that follows the rate expression

$$\text{rate} = k[Cl_2][H_2S]$$

Which, if any, of the following mechanisms are consistent with the observed rate expression?

(a) $Cl_2 + H_2S \longrightarrow H^+ + Cl^- + Cl^+ + HS^-$ (slow)
$Cl^+ + HS^- \longrightarrow H^+ + Cl^- + S$ (fast)

(b) $H_2S \rightleftharpoons HS^- + H^+$ (fast equilibrium)
$HS^- + Cl_2 \longrightarrow 2\ Cl^- + S + H^+$ (slow)

(c) $H_2S \rightleftharpoons HS^- + H^+$ (fast equilibrium)
$H^+ + Cl_2 \rightleftharpoons H^+ + Cl^- + Cl^+$ (fast equilibrium)
$Cl^+ + HS^- \longrightarrow H^+ + Cl^- + S$ (slow)

29. Nitryl chloride is a reactive gas with a normal boiling point of −16°C. Its decomposition to nitrogen dioxide and chlorine is described by the equation

$$2\ NO_2Cl \longrightarrow 2\ NO_2 + Cl_2$$

The rate expression for this reaction has the form

$$\text{rate} = k[NO_2Cl]$$

Which, if any, of the following mechanisms are consistent with the observed rate expression?

(a) $NO_2Cl \longrightarrow NO_2 + Cl$ (slow)
$Cl + NO_2Cl \longrightarrow NO_2 + Cl_2$ (fast)

(b) $2\ NO_2Cl \rightleftharpoons N_2O_4 + Cl_2$ (fast equilibrium)
$N_2O_4 \longrightarrow 2\ NO_2$ (slow)

(c) $2\ NO_2Cl \rightleftharpoons ClO_2 + N_2O + ClO$ (fast equilibrium)
$N_2O + ClO_2 \rightleftharpoons NO_2 + NOCl$ (fast equilibrium)
$NOCl + ClO \longrightarrow NO_2 + Cl_2$ (slow)

30. Ozone in the upper atmosphere is decomposed by nitrogen oxide through the reaction

$$O_3 + NO \longrightarrow O_2 + NO_2$$

The experimental rate expression for this reaction is

$$\text{rate} = k[O_3][NO]$$

Which, if any, of the following mechanisms are consistent with the observed rate expression?

(a) $O_3 + NO \longrightarrow O + NO_3$ (slow)
$O + O_3 \longrightarrow 2\ O_2$ (fast)
$NO_3 + NO \longrightarrow 2\ NO_2$ (fast)

(b) $O_3 + NO \longrightarrow O_2\ NO_2$ (slow)

(c) $NO + NO \rightleftharpoons N_2O_2$ (fast equilibrium)
$N_2O_2 + O_3 \longrightarrow NO_2 + 2\ O_2$ (slow)

31. Consider the mechanism of problem 25(a). Suppose *no* assumptions are made about the relative rates of the steps. By making a steady-state approximation for the concentration of the intermediate (C), express the rate of production of the product (F) in terms of the concentrations of A, B, D, and E. In what limit does this reduce to the result of problem 25(a)?

32. Consider the mechanism of problem 25(b). Suppose *no* assumptions are made about the relative rates of the steps. By making a steady-state approximation for the concentrations of the intermediates (C and E), express the rate of production of the product (F) in terms of the concentrations of A, B, and D. In what limit does this reduce to the result of problem 25(b)?

33. The mechanism for the decomposition of NO_2Cl is

$$NO_2Cl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + Cl$$

$$NO_2Cl + Cl \xrightarrow{k_2} NO_2 + CL_2$$

By making a steady-state approximation for [Cl], express the rate of appearance of Cl_2 in terms of the concentrations of NO_2Cl and NO_2.

34. A key step in the formation of sulfuric acid from dissolved SO_2 in acid precipitation is the oxidation of hydrogen sulfite ion by hydrogen peroxide:

$$HSO_3^-(aq) + H_2O_2(aq) \longrightarrow HSO_4^-(aq) + H_2O(\ell)$$

The mechanism involves peroxymonosulfurous acid, SO_2OOH^-:

$$HSO_3^-(aq) + H_2O_2(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} SO_2OOH^-(aq) + H_2O(\ell)$$

$$SO_2OOH^-(aq) + H_3O^+(aq) \xrightarrow{k_2} HSO_4^-(aq) + H_3O^+(aq)$$

By making a steady-state approximation for the reactive intermediate concentration, $[SO_2OOH^-(aq)]$, express the rate of formation of $HSO_4^-(aq)$ in terms of the concentrations of $HSO_3^-(aq)$, $H_2O_2(aq)$, and $H_3O^+(aq)$.

Effect of Temperature on Reaction Rates

35. The rate of the elementary reaction

$$Ar + O_2 \longrightarrow Ar + O + O$$

has been studied as a function of temperature between 5000 and 18,000 K. The following data were obtained for the rate constant *k:*

Temperature (K)	k (L mol^{-1} s^{-1})
5,000	5.49×10^6
10,000	9.86×10^8
15,000	5.09×10^9
18,000	8.60×10^9

(a) Calculate the activation energy of this reaction.
(b) Calculate the factor *A* in the Arrhenius equation for the temperature dependence of the rate constant.

36. The gas-phase reaction

$$H + D_2 \longrightarrow HD + D$$

is the exchange of isotopes of hydrogen of atomic mass 1 (H) and 2 (D, deuterium). The following data were obtained for the rate constant *k* of this reaction:

Temperature (K)	k (L mol^{-1} s^{-1})
299	1.56×10^4
327	3.77×10^4
346	7.6×10^4
440	10^6
549	1.07×10^6
745	8.7×10^7

(a) Calculate the activation energy of this reaction.
(b) Calculate the factor *A* in the Arrhenius equation for the temperature dependence of the rate constant.

37. The rate constant of the elementary reaction

$$BH_4^-(aq) + NH_4^+(aq) \longrightarrow BH_3NH_3(aq) + H_2(g)$$

is $k = 1.94 \times 10^{-4}$ L mol^{-1} s^{-1} at 30.0°C, and the reaction has an activation energy of 161 kJ mol^{-1}.
(a) Compute the rate constant of the reaction at a temperature of 40.0°C.
(b) After equal concentrations of $BH_4^-(aq)$ and $NH_4^-(aq)$ are mixed at 30.0°C, 1.00×10^4 s is required for half of them to be consumed. How long will it take to consume half of the reactants if an identical experiment is performed at 40.0°C?

38. Dinitrogen tetraoxide (N_2O_4) decomposes spontaneously at room temperature in the gas phase:

$$N_2O_4(g) \longrightarrow 2\ NO_2(g)$$

The rate law governing the disappearance of N_2O_4 with time is

$$-\frac{d[N_2O_4]}{dt} = k[N_2O_4]$$

At 30°C, $k = 5.1 \times 10^6$ s^{-1} and the activation energy for the reaction is 54.0 kJ mol^{-1}.
(a) Calculate the time (in seconds) required for the partial pressure of $N_2O_4(g)$ to decrease from 0.10 atm to 0.010 atm at 30°C.
(b) Repeat the calculation of part (a) at 300°C.

39. The activation energy for the isomerization reaction of CH_3NC in Problem 14 is 161 kJ mol^{-1}, and the reaction rate constant at 600 K is 0.41 s^{-1}.
(a) Calculate the Arrhenius factor *A* for this reaction.
(b) Calculate the rate constant for this reaction at 1000 K.

40. Cyclopropane isomerizes to propylene according to a first-order reaction:

$$\text{cyclopropane} \longrightarrow \text{propylene}$$

The activation energy is $E_a = 272$ kJ mol^{-1}. At 500°C, the reaction rate constant is 6.1×10^{-4} s^{-1}.
(a) Calculate the Arrhenius factor *A* for this reaction.
(b) Calculate the rate constant for this reaction at 25°C.

41. The activation energy of the gas-phase reaction

$$OH(g) + HCl(g) \longrightarrow H_2O(g) + Cl(g)$$

is 3.5 kJ mol^{-1}, and the change in the internal energy in the reaction is $\Delta U = -66.8$ kJ mol^{-1}. Calculate the activation energy of the reaction

$$H_2O(g) + Cl(g) \longrightarrow OH(g) + HCl(g)$$

42. The compound HOCl is known, but the related compound HClO, with a different order for the atoms in the molecule, is not known. Calculations suggest that the activation energy for the conversion HOCl ⟶ HClO is 311 kJ mol^{-1} and that for the conversion HClO ⟶ HOCl is 31 kJ mol^{-1}. Estimate ΔU for the reaction HOCl ⟶ HClO.

Reaction Dynamics

43. Use collision theory to estimate the preexponential factor in the rate constant for the elementary reaction

$$NOCl + NOCl \longrightarrow 2\ NO + Cl_2$$

at 25°C. Take the average diameter of an NOCl molecule to be 3.0×10^{-10} m and use the steric factor *P* from Table 18.1.

44. Use collision theory to estimate the preexponential factor in the rate constant for the elementary reaction

$$NO_2 + NO_2 \longrightarrow 2\ NO + O_2$$

at 500 K. Take the average diameter of an NO_2 molecule to be 2.6×10^{-10} m and use the steric factor *P* from Table 18.1.

Kinetics of Catalysis

45. Certain bacteria use the enzyme penicillinase to decompose penicillin and render it inactive. The Michaelis–Menten constants for this enzyme and substrate are $K_m = 5 \times 10^{-5}$ mol L^{-1} and $k_2 = 2 \times 10^3$ s^{-1}.

(a) What is the maximum rate of decomposition of penicillin if the enzyme concentration is 6×10^{-7} M?

(b) At what substrate concentration will the rate of decomposition be half that calculated in part (a)?

46. The conversion of dissolved carbon dioxide in blood to HCO_3^- and H_3O^+ is catalyzed by the enzyme carbonic anhydrase. The Michaelis–Menten constants for this enzyme and substrate are $K_m = 8 \times 10^{-5}$ mol L^{-1} and $k_2 = 6 \times 10^5$ s^{-1}.

(a) What is the maximum rate of reaction of carbon dioxide if the enzyme concentration is 5×10^{-6} M?

(b) At what CO_2 concentration will the rate of decomposition be 30% of that calculated in part (a)?

ADDITIONAL PROBLEMS

47. Hemoglobin molecules in blood bind oxygen and carry it to cells, where it takes part in metabolism. The binding of oxygen

$$\text{hemoglobin}(aq) + O_2(aq) \longrightarrow \text{hemoglobin}\cdot O_2(aq)$$

is first order in hemoglobin and first order in dissolved oxygen, with a rate constant of 4×10^7 L mol^{-1} s^{-1}. Calculate the initial rate at which oxygen will be bound to hemoglobin if the concentration of hemoglobin is 2×10^{-9} M and that of oxygen is 5×10^{-5} M.

* **48.** Suppose 1.00 L of 9.95×10^{-3} M $S_2O_3^{2-}$ is mixed with 1.00 L of 2.52×10^{-3} M H_2O_2 at a pH of 7.0 and a temperature of 25°C. These species react by two competing pathways, represented by the balanced equations

$$S_2O_3^{2-} + 4\ H_2O_2 \longrightarrow 2\ SO_4^{2-} + H_2O + 2\ H_3O^+$$

$$2\ S_2O_3^{2-} + H_2O_2 + 2\ H_3O^+ \longrightarrow S_4O_6^{2-} + 4\ H_2O$$

At the instant of mixing, the thiosulfate ion ($S_2O_3^{2-}$) is observed to be disappearing at the rate of 7.9×10^{-7} mol L^{-1} s^{-1}. At the same moment, the H_2O_2 is disappearing at the rate of 8.8×10^{-7} mol L^{-1} s^{-1}.

(a) Compute the percentage of the $S_2O_3^{2-}$ that is, at that moment, reacting according to the first equation.

(b) It is observed that the hydronium ion concentration drops. Use the data and answer from part (a) to compute how many milliliters per minute of 0.100 M H_3O^+ must be added to keep the pH equal to 7.0.

49. 8.23×10^{-3} mol of InCl(*s*) is placed in 1.00 L of 0.010 M HCl(*aq*) at 75°C. The InCl(*s*) dissolves quite quickly, and then the following reaction occurs:

$$3\ In^+(aq) \longrightarrow 2\ In(s) + In^{3+}(aq)$$

As this disproportionation proceeds, the solution is analyzed at intervals to determine the concentration of $In^+(aq)$ that remains.

Time (s)	[In$^+$] (mol L^{-1})
0	8.23×10^{-3}
240	6.41×10^{-3}
480	5.00×10^{-3}
720	3.89×10^{-3}
1000	3.03×10^{-3}
1200	3.03×10^{-3}
10,000	3.03×10^{-3}

(a) Plot ln [In$^+$] versus time, and determine the apparent rate constant for this first-order reaction.

(b) Determine the half-life of this reaction.

(c) Determine the equilibrium constant *K* for the reaction under the experimental conditions.

* **50.** A compound called di-*t*-butyl peroxide [abbreviation DTBP, formula $(CH_3)_3COOC(CH_3)_3$] decomposes to give acetone [$(CH_3)_2CO$] and ethane (C_2H_6):

$$(CH_3)_3COOC(CH_3)_3(g) \longrightarrow 2\ (CH_3)_2CO(g) + C_2H_6(g)$$

The *total* pressure of the reaction mixture changes with time, as shown by the following data at 147.2°C:

Time (min)	P_{tot} (atm)	Time (min)	P_{tot} (atm)
0	0.2362	26	0.3322
2	0.2466	30	0.3449
6	0.2613	34	0.3570
10	0.2770	38	0.3687
14	0.2911	40	0.3749
18	0.3051	42	0.3801
20	0.3122	46	0.3909
22	0.3188		

(a) Calculate the partial pressure of DTBP at each time from these data. Assume that at time 0, DTBP is the only gas present.

(b) Are the data better described by a first-order or a second-order rate expression with respect to DTBP concentration?

51. The reaction of OH^- with HCN in aqueous solution at 25°C has a forward rate constant k_f of 3.7×10^9 L mol^{-1} s^{-1}. Using this information and the measured acid ionization constant of HCN (see Table 15.2), calculate the rate constant k_r in the first-order rate law rate = $k_r[CN^-]$ for the transfer of hydrogen ions to CN^- from surrounding water molecules:

$$H_2O(\ell) + CN^-(aq) \longrightarrow OH^-(aq) + HCN(aq)$$

52. Carbon dioxide reacts with ammonia to give ammonium carbamate, a solid. The reverse reaction also occurs:

$$CO_2(g) + 2\ NH_3(g) \rightleftharpoons NH_4OCONH_2(s)$$

The forward reaction is first order in $CO_2(g)$ and second order in $NH_3(g)$. Its rate constant is 0.238 atm^{-2} s^{-1} at

0.0°C (expressed in terms of partial pressures rather than concentrations). The reaction in the reverse direction is zero order, and its rate constant, at the same temperature, is 1.60×10^{-7} atm s^{-1}. Experimental studies show that, at all stages in the progress of this reaction, the net rate is equal to the forward rate minus the reverse rate. Compute the equilibrium constant of this reaction at 0.0°C.

53. For the reactions

$$\mathrm{I + I + M \longrightarrow I_2 + M}$$

$$\mathrm{Br + Br + M \longrightarrow Br_2 + M}$$

the rate laws are

$$-\frac{d[\mathrm{I}]}{dt} = k_{\mathrm{I}}[\mathrm{I}]^2[\mathrm{M}]$$

$$-\frac{d[\mathrm{Br}]}{dt} = k_{\mathrm{Br}}[\mathrm{Br}]^2[\mathrm{M}]$$

The ratio $k_{\mathrm{I}}/k_{\mathrm{Br}}$ at 500°C is 3.0 when M is an Ar molecule. Initially, $[\mathrm{I}]_0 = 2[\mathrm{Br}]_0$, while [M] is the same for both reactions and is much greater than $[\mathrm{I}]_0$. Calculate the ratio of the time required for [I] to decrease to half its initial value to the same time for [Br] at 500°C.

54. In some reactions there is a competition between kinetic control and thermodynamic control over product yields. Suppose compound A can undergo two elementary reactions to stable products:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \quad \text{or} \quad \mathrm{A} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{C}$$

For simplicity we assume first-order kinetics for both forward and reverse reactions. We take the numerical values $k_1 = 1 \times 10^8\ \mathrm{s}^{-1}$, $k_{-1} = 1 \times 10^2\ \mathrm{s}^{-1}$, $k_2 = 1 \times 10^9\ \mathrm{s}^{-1}$, and $k_{-2} = 1 \times 10^4\ \mathrm{s}^{-1}$.

(a) Calculate the equilibrium constant for the equilibrium

$$\mathrm{B} \rightleftharpoons \mathrm{C}$$

From this value, give the ratio of the concentration of B to that of C at equilibrium. This is an example of thermodynamic control.

(b) In the case of kinetic control, the products are isolated (or undergo additional reaction) before the back reactions can take place. Suppose the back reactions in the preceding example (k_{-1} and k_{-2}) can be ignored. Calculate the concentration ratio of B to C reached in this case.

55. Compare and contrast the mechanisms for the two gas-phase reactions

$$\mathrm{H_2 + Br_2 \longrightarrow 2\,HBr}$$

$$\mathrm{H_2 + I_2 \longrightarrow 2\,HI}$$

56. In Section 18.4 the steady-state approximation was used to derive a rate expression for the decomposition of $\mathrm{N_2O_5}(g)$:

$$\text{rate} = \frac{k_1 k_2[\mathrm{M}][\mathrm{N_2O_5}]}{k_2 + k_{-1}[\mathrm{M}]} = k_{\mathrm{eff}}[\mathrm{N_2O_5}]$$

At 300 K, with an excess of nitrogen present, the following values of k_{eff} as a function of total pressure were found:

P (atm)	**k_{eff}(s^{-1})**	**P (atm)**	**k_{eff} (s^{-1})**
9.21	0.265	0.625	0.116
5.13	0.247	0.579	0.108
3.16	0.248	0.526	0.104
3.03	0.223	0.439	0.092
		0.395	0.086

Use the data to estimate the value of k_{eff} at very high total pressure and the value of k_1 in L mol^{-1} s^{-1}.

57. The decomposition of ozone by light can be described by the mechanism

$$\mathrm{O_3 + light} \xrightarrow{k_1} \mathrm{O_2 + O}$$

$$\mathrm{O + O_2 + M} \xrightarrow{k_2} \mathrm{O_3 + M}$$

$$\mathrm{O + O_3} \xrightarrow{k_3} \mathrm{2\,O_2}$$

with the overall reaction being

$$\mathrm{2\,O_3 + light \longrightarrow 3\,O_2}$$

The rate constant k_1 depends on the light intensity and the type of light source used. By making a steady-state approximation for the concentration of oxygen atoms, express the rate of formation of $\mathrm{O_2}$ in terms of the $\mathrm{O_2}$, $\mathrm{O_3}$, and M concentrations and the elementary rate constants. Show that only the ratio k_3/k_2, and not the individual values of k_2 and k_3, affects the rate.

*** 58.** In Section 18.4 we considered the following mechanism for the reaction of $\mathrm{Br_2}$ with $\mathrm{H_2}$:

$$\mathrm{Br_2 + M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Br + Br + M}$$

$$\mathrm{Br + H_2} \xrightarrow{k_2} \mathrm{HBr + H}$$

$$\mathrm{H + Br_2} \xrightarrow{k_3} \mathrm{HBr + Br}$$

Although this is adequate for calculating the *initial* rate of reaction, before product HBr builds up, there is an additional process that can participate as the reaction continues:

$$\mathrm{HBr + H} \xrightarrow{k_4} \mathrm{H_2 + Br}$$

(a) Write an expression for the rate of change of [H].

(b) Write an expression for the rate of change of [Br].

(c) As hydrogen and bromine atoms are both short-lived species, we can make the steady-state approximation and set the rates from parts (a) and (b) to 0. Express the steady-state concentrations [H] and [Br] in terms of concentrations of $\mathrm{H_2}$, $\mathrm{Br_2}$, HBr, and M. [*Hint:* Try adding the rate for part (a) to that for part (b).]

(d) Express the rate of production of HBr in terms of concentrations of $\mathrm{H_2}$, $\mathrm{Br_2}$, HBr, and M.

59. The following observations have been made about a certain reacting system: (i) When A, B, and C are mixed at about equal concentrations in neutral solution, two different products are formed, D and E, with the amount of D about 10 times as great as the amount of E. (ii) If everything is done as in (i) except that a trace of acid is added to the reaction mixture, the same products are formed, except that now the amount of D produced is much smaller than (about 1% of) the amount of E. The acid is not consumed in the reaction. The following mechanism has been proposed to account for some of these observations and others about the order of the reactions:

(1) $\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_2}{\rightleftarrows}} \mathrm{F}$ (rapid equilibrium)

(2) $\mathrm{C} + \mathrm{F} \xrightarrow{k_2} \mathrm{D}$ (negligible reverse rate)

(3) $\mathrm{C} + \mathrm{F} \xrightarrow{k_3} \mathrm{E}$ (negligible reverse rate)

(a) Explain what this proposed scheme of reactions implies about the dependence (if any) of the rate of formation of D on the concentrations of A, of B, and of C. What about the dependence (if any) of the rate of formation of E on these same concentrations? (b) What can you say about the relative magnitudes of k_2 and k_3? (c) What explanation can you give for observation (ii) in view of your answer to (b)?

60. Iron(II) ion is oxidized by chlorine in aqueous solution, the overall equation being

$$2\,\mathrm{Fe}^{2+} + \mathrm{Cl}_2 \longrightarrow 2\,\mathrm{Fe}^{3+} + 2\,\mathrm{Cl}^-$$

It is found experimentally that the rate of the overall reaction is decreased when either the iron(III) ion or the chloride-ion concentration is increased. Which of the following possible mechanisms is consistent with the experimental observations?

(a) (1) $\mathrm{Fe}^{2+} + \mathrm{Cl}_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Fe}^{3+} + \mathrm{Cl}^- + \mathrm{Cl}$ (rapid equilibrium)

(2) $\mathrm{Fe}^{2+} + \mathrm{Cl} \xrightarrow{k_2} \mathrm{Fe}^{3+} + \mathrm{Cl}^-$ (negligible reverse rate)

(b) (3) $\mathrm{Fe}^{2+} + \mathrm{Cl}_2 \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{Fe(IV)} + 2\,\mathrm{Cl}^-$ (rapid equilibrium)

(4) $\mathrm{Fe(IV)} + \mathrm{Fe}^{2+} \xrightarrow{k_4} 2\,\mathrm{Fe}^{3+}$ (negligible reverse rate)

where Fe(IV) is Fe in the (+IV) oxidation state.

61. Manfred Eigen, a German physical chemist working during the 1970s and 1980s, earned a Nobel Prize for developing the "temperature-jump" method for studying kinetics of very rapid reactions in solution, such as proton transfer. Eigen and his co-workers found that the specific rate of proton transfer from a water molecule to an ammonia molecule in a dilute aqueous solution is $k = 2 \times 10^5\ \mathrm{s}^{-1}$. The equilibrium constant K_b for the reaction of ammonia with water is 1.8×10^{-5} M. What, if anything, can be deduced from this information about the rate of transfer of a proton from NH_4^+ to a hydroxide ion? Write equations for any reactions you mention, making it clear to which reaction(s) any quoted constant(s) apply.

62. Consider the reaction

$$\mathrm{A} + \mathrm{B} \rightleftarrows \mathrm{C} + \mathrm{D}$$

with all reactants and products gaseous (for simplicity) and an equilibrium constant K. (a) Assume that the elementary steps in the reaction are those indicated by the stoichiometric equation (in each direction), with specific rate constants for the forward reaction and the reverse reaction, respectively, k_f and k_r. Derive the relation between k_f, k_r, and K. Comment on the general validity of the assumptions made about the relation of elementary steps and the stoichiometric equation and also on the general validity of K. (b) Assume that the reaction as written is exothermic. Explain what this implies about the change of K with temperature. Explain also what it implies about the relation of the activation energies of the forward and reverse reactions and how this relation is consistent with your statement about the variation of K with temperature.

63. The gas-phase decomposition of acetaldehyde can be represented by the overall chemical equation

$$\mathrm{CH_3CHO} \longrightarrow \mathrm{CH_4} + \mathrm{CO}$$

It is thought to occur through the sequence of reactions

$$\mathrm{CH_3CHO} \longrightarrow \mathrm{CH_3} + \mathrm{CHO}$$

$$\mathrm{CH_3} + \mathrm{CH_3CHO} \longrightarrow \mathrm{CH_4} + \mathrm{CH_2CHO}$$

$$\mathrm{CH_2CHO} \longrightarrow \mathrm{CO} + \mathrm{CH_3}$$

$$\mathrm{CH_3} + \mathrm{CH_3} \longrightarrow \mathrm{CH_3CH_3}$$

Show that this reaction mechanism corresponds to a chain reaction, and identify the initiation, propagation, and termination steps.

64. Lanthanum(III) phosphate crystallizes as a hemihydrate, $\mathrm{LaPO_4{\cdot}\frac{1}{2}\,H_2O}$. When it is heated, it loses water to give anhydrous lanthanum(III) phosphate:

$$2(\mathrm{LaPO_4{\cdot}\tfrac{1}{2}\,H_2O}(s)) \longrightarrow 2\,\mathrm{LaPO_4}(s) + \mathrm{H_2O}(g)$$

This reaction is first order in the chemical amount of $\mathrm{LaPO_4{\cdot}\frac{1}{2}\,H_2O}$. The rate constant varies with temperature as follows:

Temperature (°C)	k (s^{-1})
205	2.3×10^{-4}
219	3.69×10^{-4}
246	7.75×10^{-4}
260	12.3×10^{-4}

Compute the activation energy of this reaction.

65. The water in a pressure cooker boils at a temperature greater than 100°C because it is under pressure. At this higher temperature, the chemical reactions associated with the cooking of food take place at a greater rate.

(a) Some food cooks fully in 5 min in a pressure cooker at 112°C and in 10 minutes in an open pot at 100°C. Calculate the average activation energy for the reactions associated with the cooking of this food.

(b) How long will the same food take to cook in an open pot of boiling water in Denver, where the average atmospheric pressure is 0.818 atm and the boiling point of water is 94.4°C?

66. (a) A certain first-order reaction has an activation energy of 53 kJ mol^{-1}. It is run twice, first at 298 K and then at 308 K (10°C higher). All other conditions are identical. Show that, in the second run, the reaction occurs at double its rate in the first run.
(b) The same reaction is run twice more at 398 K and 408 K. Show that the reaction goes 1.5 times as fast at 408 K as it does at 398 K.

* 67. The gas-phase reaction between hydrogen and iodine

$$H_2(g) + I_2(g) \underset{k_r}{\overset{k_f}{\rightleftarrows}} 2\ HI(g)$$

proceeds with a forward rate constant at 1000 K of $k_f = 240$ L mol^{-1} s^{-1} and an activation energy of 165 kJ mol^{-1}. By using this information and data from Appendix D, calculate the activation energy for the reverse reaction and the value of k_r at 1000 K. Assume that ΔH and ΔS for the reaction are independent of temperature between 298 and 1000 K.

68. The following reaction mechanism has been proposed for a chemical reaction:

$$A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A + A \qquad \text{(fast equilibrium)}$$

$$A + B \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} AB \qquad \text{(fast equilibrium)}$$

$$AB + CD \xrightarrow{k_3} AC + BD \qquad \text{(slow)}$$

(a) Write a balanced equation for the overall reaction.
(b) Write the rate expression that corresponds to the preceding mechanism. Express the rate in terms of concentrations of reactants only (A_2, B, CD).
(c) Suppose that the first two steps in the preceding mechanism are endothermic and the third one is exothermic. Will an increase in temperature increase the reaction rate constant, decrease it, or cause no change? Explain.

69. How would you describe the role of the CF_2Cl_2 in the reaction mechanism of Problem 21?

70. In Section 18.7 we wrote a mechanism in which silver ions catalyze the reaction of Tl^+ with Ce^{4+}. Determine the rate law for this mechanism by making a steady-state approximation for the concentration of the reactive intermediate Ag^{2+}.

71. The rates of enzyme catalysis can be lowered by the presence of inhibitor molecules I, which bind to the active site of the enzyme. This adds the following additional step to the reaction mechanism considered in Section 18.7:

$$E + I \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} EI \qquad \text{(fast equilibrium)}$$

Determine the effect of the presence of inhibitor at total concentration $[I]_0 = [I] + [EI]$ on the rate expression for formation of products derived at the end of this chapter.

72. The enzyme lysozyme kills certain bacteria by attacking a sugar called *N*-acetylglucosamine (NAG) in their cell walls. At an enzyme concentration of 2×10^{-6} M, the maximum rate for substrate (NAG) reaction, found at high substrate concentration, is 1×10^{-6} mol L^{-1} s^{-1}. The rate is reduced by a factor of 2 when the substrate concentration is reduced to 6×10^{-6} M. Determine the Michaelis–Menten constants K_m and k_2 for lysozyme.

CUMULATIVE PROBLEMS

73. The rate of the gas-phase reaction

$$H_2 + I_2 \longrightarrow 2\ HI$$

is given by

$$\text{rate} = -\frac{d[I_2]}{dt} = k[H_2][I_2]$$

with $k = 0.0242$ L mol^{-1} s^{-1} at 400°C. If the initial concentration of H_2 is 0.081 mol L^{-1} and that of I_2 is 0.036 mol L^{-1}, calculate the initial rate at which heat is absorbed or emitted during the reaction. Assume that the enthalpy change at 400°C is the same as that at 25°C.

74. The rate of the reaction

$$2\ ClO_2(aq) + 2\ OH^-(aq) \longrightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(\ell)$$

is given by

$$\text{rate} = k[ClO_2]^2[OH^-]$$

with $k = 230$ L^2 mol^{-2} s^{-1} at 25°C. A solution is prepared that has initial concentrations $[ClO_2] = 0.020$ M, $[HCN] = 0.095$ M, and $[CN^-] = 0.17$ M. Calculate the initial rate of the reaction.

75. A gas mixture was prepared at 500 K with total pressure 3.26 atm and a mole fraction of 0.00057 of NO and 0.00026 of O_3. The elementary reaction

$$NO + O_3 \longrightarrow NO_2 + O_2$$

has a second-order rate constant of 7.6×10^7 L mol^{-1} s^{-1} at this temperature. Calculate the initial rate of the reaction under these conditions.

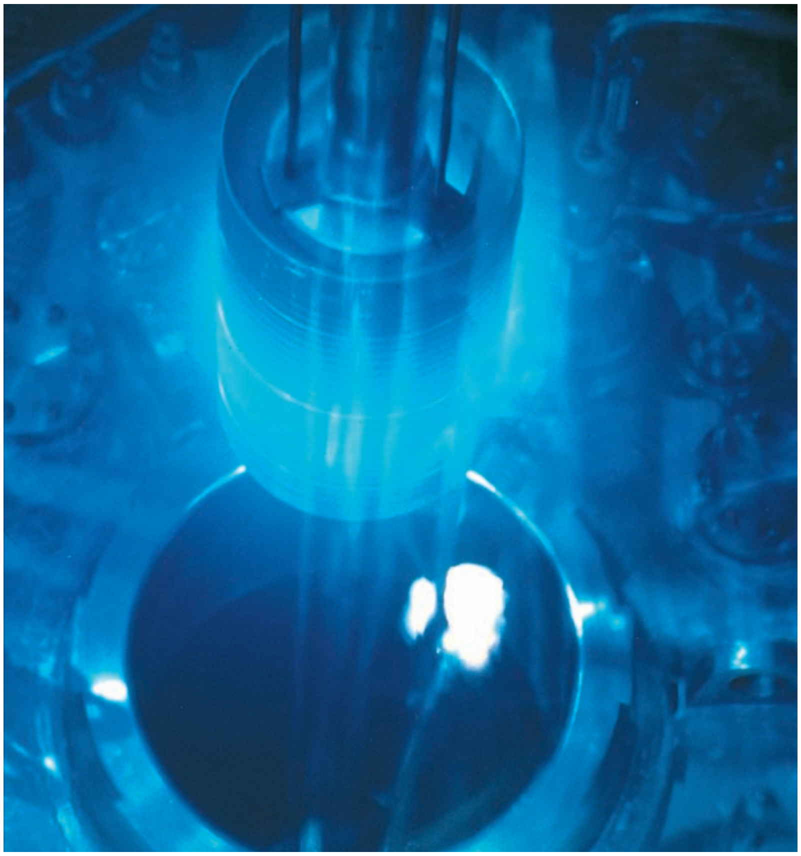
76. The activation energy for the reaction

$$2\ NO_2 \longrightarrow 2\ NO + O_2$$

is $E_a = 111$ kJ mol^{-1}. Calculate the root-mean-square velocity of an NO_2 molecule at 400 K and compare it to the velocity of an NO_2 molecule with kinetic energy E_a/N_A.

CHAPTER 19

Nuclear Chemistry



U.S. Department of Energy/Photo Researchers, Inc.

A fuel element being removed at the High Flux Isotope Reactor at Oak Ridge National Laboratory. The fuel element and the reactor head are submerged in water in this design. The blue glow is due to Cerenkov radiation, emitted by energetic charged particles traveling through the water. This 100-megawatt reactor is used to conduct research on synthetic heavy elements, and its principal product is the isotope ^{235}Cf.

In the preceding chapters, we discuss chemical reactions essentially as rearrangements of atoms from one set of “bonding partners” to another set. We turn now to a different kind of reaction in which the elemental identity of the atomic nucleus changes in the course of the reaction. This is a fascinating subject that arose early in the 20th century from experimental studies of the physical structure of the atom (see Section 1.4).

A fundamentally different new feature distinguishes this field from the material in earlier chapters. The separate laws of conservation of matter and conservation of energy must be generalized. Nuclear reactions occur at energies sufficiently high that energy and matter are interconverted. This is the origin of the enormous amounts of energy that can be released during nuclear reactions. Mass and energy are related through Einstein's relation $E = mc^2$, and their *sum* is conserved during nuclear reactions.

19.1 Mass–Energy Relationships in Nuclei

Recall from Section 1.4 that almost all the mass of an atom is concentrated in a very small volume in the nucleus. The small size of the nucleus (which occupies less than one *trillionth* of the space in the atom) and the strong forces between the protons and neutrons that make it up largely isolate its behavior from the outside world of electrons and other nuclei. This greatly simplifies our analysis of nuclear chemistry, allowing us to examine single nuclei without concern for the atoms, ions, or molecules in which they may be found.

As defined in Section 1.4, a nuclide is characterized by the number of protons, Z, and the number of neutrons, N, it contains. The atomic number Z determines the charge $+Ze$ on the nucleus and therefore decides the identity of the element; the sum $Z + N = A$ is the mass number of the nuclide and is the integer closest to the relative atomic mass of the nuclide. Nuclides are designated by the symbol ${}^{A}_{Z}X$ where X is the chemical symbol for the element.

The absolute masses of nuclides and of elementary particles such as the proton, neutron, and electron are far too small to express in kilograms or grams without the constant use of 10 raised to some large negative exponent. A unit of mass that is better sized for measuring on the submicroscopic scale is needed. An **atomic mass unit** (abbreviated u) is defined as exactly $\frac{1}{12}$ the mass of a single atom of ^{12}C. Because 1 mol of ^{12}C atoms weighs exactly 12 g, one atom weighs $12/N_A$ grams, and

$$1 \text{ u} = \frac{1}{12}\left(\frac{12 \text{ g mol}^{-1}}{6.0221420 \times 10^{23} \text{ mol}^{-1}}\right)$$
$$= 1.6605387 \times 10^{-24} \text{ g} = 1.6605387 \times 10^{-27} \text{ kg}$$

The conversion factor between atomic mass units and grams is numerically equal to the inverse of Avogadro's number N_A, and the mass of a single atom in atomic mass units is numerically equal to the mass of one mole of atoms in grams. Thus, one atom of ^{1}H has a mass of 1.007825 u because 1 mol of ^{1}H has a mass of 1.007825 g. The *dalton* is a mass unit that is equivalent to the atomic mass unit and is used frequently in biochemistry.

Table 19.1 lists the masses of elementary particles and selected neutral atoms, obtained from mass spectrometry (see Fig. 1.12). Note that each atomic mass includes the contribution from the surrounding Z electrons as well as that from the nucleus.

The Einstein Mass–Energy Relationship

Some nuclides are stable and can exist indefinitely, but others are unstable (radioactive) and decay spontaneously to form other nuclides in processes to be considered in Section 19.2. Figure 19.1 shows the distribution of the number of neutrons N ($= A - Z$) against atomic number Z (protons in the nucleus) for the known nuclides of the elements. For the light elements, $N/Z \approx 1$ for stable nuclides, meaning nearly equal numbers of protons and neutrons are found in the nucleus. For the heavier elements, $N/Z > 1$ and there are progressively more

TABLE 19.1 Masses of Selected Elementary Particles and Atoms

Elementary Particle	Symbol	Mass (u)	Mass (kg)
Electron, beta particle	${}^{0}_{-1}e^{-}$	0.000548579911	$9.1093819 \times 10^{-31}$
Positron	${}^{0}_{1}e^{+}$	0.000548579911	$9.1093819 \times 10^{-31}$
Proton	${}^{1}_{1}p^{+}$	1.0072764669	$1.6726216 \times 10^{-27}$
Neutron	${}^{1}_{0}n$	1.0086649158	$1.6749272 \times 10^{-27}$

Atom	Mass (u)	Atom	Mass (u)
${}^{1}_{1}\text{H}$	1.007825032	${}^{23}_{11}\text{Na}$	22.9897697
${}^{2}_{1}\text{H}$	2.014101778	${}^{24}_{12}\text{Mg}$	23.9850419
${}^{3}_{1}\text{H}$	3.016049268	${}^{30}_{14}\text{Si}$	29.97377022
${}^{3}_{2}\text{He}$	3.016029310	${}^{30}_{15}\text{P}$	29.9783138
${}^{4}_{2}\text{He}$	4.002603250	${}^{32}_{16}\text{S}$	31.9720707
${}^{7}_{3}\text{Li}$	7.0160040	${}^{35}_{17}\text{Cl}$	34.96885271
${}^{8}_{4}\text{Be}$	8.00530509	${}^{40}_{20}\text{Ca}$	39.9625912
${}^{9}_{4}\text{Be}$	9.0121821	${}^{49}_{22}\text{Ti}$	48.947871
${}^{10}_{4}\text{Be}$	10.0135337	${}^{81}_{35}\text{Br}$	80.916291
${}^{8}_{5}\text{B}$	8.024607	${}^{87}_{37}\text{Rb}$	86.909183
${}^{10}_{5}\text{B}$	10.0129370	${}^{87}_{38}\text{Sr}$	86.908879
${}^{11}_{5}\text{B}$	11.0093055	${}^{127}_{153}\text{I}$	126.904468
${}^{11}_{6}\text{C}$	11.011433	${}^{226}_{88}\text{Ra}$	226.025403
${}^{12}_{6}\text{C}$	12 exactly	${}^{228}_{88}\text{Ra}$	228.031064
${}^{13}_{6}\text{C}$	13.003354838	${}^{228}_{89}\text{Ac}$	228.031015
${}^{14}_{6}\text{C}$	14.003241988	${}^{232}_{90}\text{Th}$	232.038050
${}^{14}_{7}\text{N}$	14.003074005	${}^{234}_{90}\text{Th}$	234.043595
${}^{16}_{8}\text{O}$	15.994914622	${}^{231}_{91}\text{Pa}$	231.035879
${}^{17}_{8}\text{O}$	16.9991315	${}^{231}_{92}\text{U}$	231.036289
${}^{18}_{8}\text{O}$	17.999160	${}^{234}_{92}\text{U}$	234.040945
${}^{19}_{9}\text{F}$	18.9984032	${}^{235}_{92}\text{U}$	235.043923
${}^{21}_{11}\text{Na}$	20.99764	${}^{238}_{92}\text{U}$	238.050783

neutrons than protons in the nucleus. One of the goals of nuclear chemistry is to understand the differing stabilities of the isotopes. Nuclear mass provides the key to this understanding.

Note from Table 19.1 that the neutron has a slightly greater mass than the proton. The neutron is stable inside a nucleus, but in free space it is unstable, decaying into a proton and an electron with a half-life of about 12 minutes:

$${}^{1}_{0}n \longrightarrow {}^{1}_{1}p^{+} + {}^{0}_{-1}e^{-}$$

Here ${}^{1}_{0}n$ and ${}^{1}_{1}p^{+}$ represent the neutron and the proton, respectively. We have written this as a **balanced nuclear equation.** To check such an equation for balance, first verify that the total mass numbers (the superscripts) are equal on the two sides. Then verify that the nuclear charges are balanced by checking the sum of the subscripts.

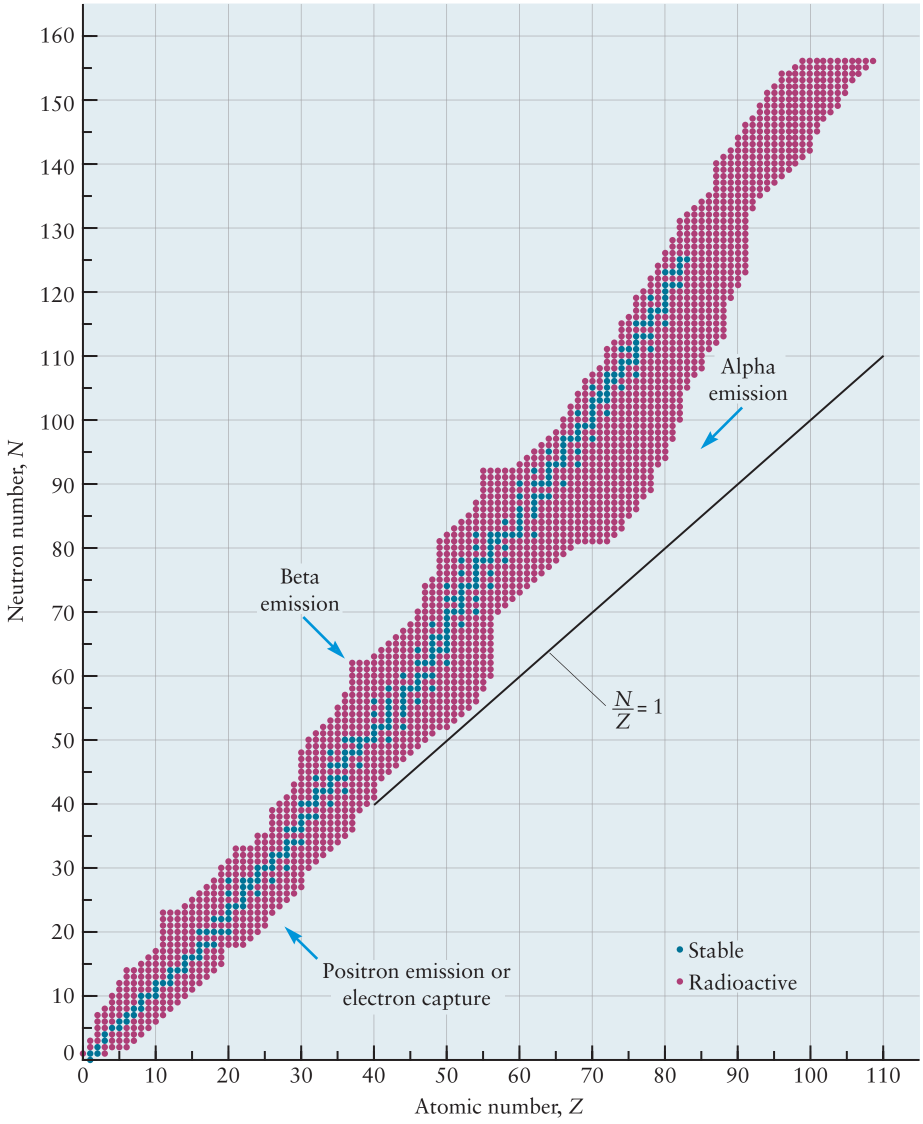
Mass is not conserved in the reaction just written. By subtracting the mass of the reactant from the masses of the products (using Table 19.1), the change in mass is calculated to be

$$\Delta m = -1.3947 \times 10^{-30}\ \text{kg} = -8.398690 \times 10^{-4}\ \text{u}$$

What has happened to the "lost" mass? It has been converted to energy—specifically, kinetic energy carried off by the electron and proton. According to Einstein's special theory of relativity, a change in mass always accompanies a change in energy:

$$E = mc^2$$

FIGURE 19.1 A plot of *N* versus *Z* for nuclides (represented by dots). Arrows show the directions of decay of unstable nuclides via alpha emission, beta emission, positron emission, or electron capture.



or, better,

$$\Delta E = c^2 \, \Delta m \qquad [19.1]$$

where c is the speed of light in a vacuum and Δm is the change in mass (mass of products minus mass of reactants). To express ΔE in joules, c must have units of meters per second, and Δm, units of kilograms. In the decay of one neutron, for example,

$$\Delta E = c^2 \, \Delta m = (2.9979 \times 10^8 \text{ m s}^{-1})^2(-1.3947 \times 10^{-30} \text{ kg}) = -1.2535 \times 10^{-13} \text{ J}$$

In ordinary chemical reactions, the change in mass is negligibly small. In the combustion of 1 mol of carbon to CO_2, the energy change is about 400 kJ, corresponding to a change in mass of only 4×10^{-9} g.

Changes in energy in nuclear reactions are nearly always expressed in more convenient energy units than the joule—namely, the **electron volt** (eV) and the **million electron volt** (MeV). The electron volt is defined as the energy given to an electron when it is accelerated through a potential difference of exactly 1 V:

$$\Delta E \text{ (joules)} = \mathcal{Q}\text{(coulombs)} \times \Delta\mathcal{E}\text{(volts)}$$

$$1 \text{ eV} = 1.60217646 \times 10^{-19} \text{ C} \times 1 \text{ V} = 1.60217646 \times 10^{-19} \text{ J}$$

The million electron volt is 1 million times larger:

$$1 \text{ MeV} = 1.60217646 \times 10^{-13} \text{ J}$$

A change in mass of 1 u = $1.6605387 \times 10^{-27}$ kg corresponds to

$$\begin{aligned}\Delta E = c^2\,\Delta m &= (2.9979246 \times 10^{8} \text{ m s}^{-1})^2(1.6605387 \times 10^{-27} \text{ kg}) \\ &= 1.4924178 \times 10^{-10} \text{ J}\end{aligned}$$

Converting to MeV,

$$\frac{1.4924178 \times 10^{-10} \text{ J}}{1.60217646 \times 10^{-13} \text{ J MeV}^{-1}} = 931.494 \text{ MeV}$$

We say that the **energy equivalent** of 1 u is 931.494 MeV. In the decay of a neutron,

$$\Delta E = (-8.39869 \times 10^{-4} \text{ u})(931.494 \text{ MeV u}^{-1}) = 0.782 \text{ MeV}$$

Binding Energies of Nuclei

The **binding energy** E_B of a nucleus is defined as the negative of the energy change ΔE that would occur if that nucleus were formed from its component protons and neutrons. For the $^4_2$He nucleus, for example,

$$2\,^1_1p^+ + 2\,^1_0n \longrightarrow \,^4_2\text{He}^{2+} \qquad \Delta E = ?$$

Binding energies of nuclei are calculated with Einstein's relationship and accurate data from a mass spectrometer. Most measurements determine the mass of the atom with most or all of its electrons, not the mass of the bare nucleus (recall that it is the ^{12}C *atom*, not the ^{12}C nucleus, that is defined to have atomic mass 12). Therefore, we take the nuclear binding energy E_B of the helium nucleus to be the negative of the energy change ΔE for the formation of an *atom* of helium from hydrogen *atoms* and neutrons.

$$2\,^1_1\text{H} + 2\,^1_0n \longrightarrow \,^4_2\text{He}$$

The correction for the differences in binding energies of electrons (which of course are present both in the hydrogen atoms and in the atom being formed) is a very small one that need not concern us here.

EXAMPLE 19.1

Calculate the binding energy of ^{4}He from the data in Table 19.1, and express it both in joules and in million electron volts (MeV).

SOLUTION

The mass change is

$$\begin{aligned}\Delta m &= m[^4_2\text{He}] - 2m[^1_1\text{H}] - 2m[^1_0n] \\ &= 4.00260325 - 2(1.00782503) - 2(1.00866492) = -0.03037665 \text{ u}\end{aligned}$$

Einstein's relation then gives

$$\begin{aligned}\Delta E &= (-0.03037665 \text{ u})(1.6605387 \times 10^{-27} \text{ kg u}^{-1})(2.9979246 \times 10^{8} \text{ m s}^{-1})^2 \\ &= -4.533465 \times 10^{-12} \text{ J} \\ E_B &= 4.533465 \times 10^{-12} \text{ J}\end{aligned}$$

If 1 *mol* of $^4_2$He atoms were formed in this way, the energy change would be greater by a factor of Avogadro's number N_A, giving $\Delta E = -2.73 \times 10^{12}$ J mol^{-1}. This is an enormous quantity, seven orders of magnitude greater than typical energy changes in chemical reactions.

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The energy change, in MeV, accompanying the formation of a ${}^{4}_{2}\mathrm{He}$ atom is

$$\Delta E = (-0.03037665\ \mathrm{u})(931.494\ \mathrm{MeV\ u^{-1}}) = -28.2957\ \mathrm{MeV}$$

Related Problems: 3, 4

There are four nucleons in the ${}^{4}_{2}\mathrm{He}$ nucleus, so the binding energy *per nucleon* is

$$\frac{E_{\mathrm{B}}}{4} = \frac{28.2957\ \mathrm{MeV}}{4} = 7.07392\ \mathrm{MeV}$$

The binding energy per nucleon is a direct measure of the stability of the nucleus. It varies with atomic number among the stable elements, increasing to a maximum of about 8.8 MeV for iron and nickel, as Figure 19.2 illustrates.

19.2 Nuclear Decay Processes

Why are some nuclei **radioactive,** decaying spontaneously, when others are stable? Thermodynamics gives the criterion $\Delta G < 0$ for a process to be spontaneous at constant T and P. The energy change ΔE in a nuclear decay process is so great that

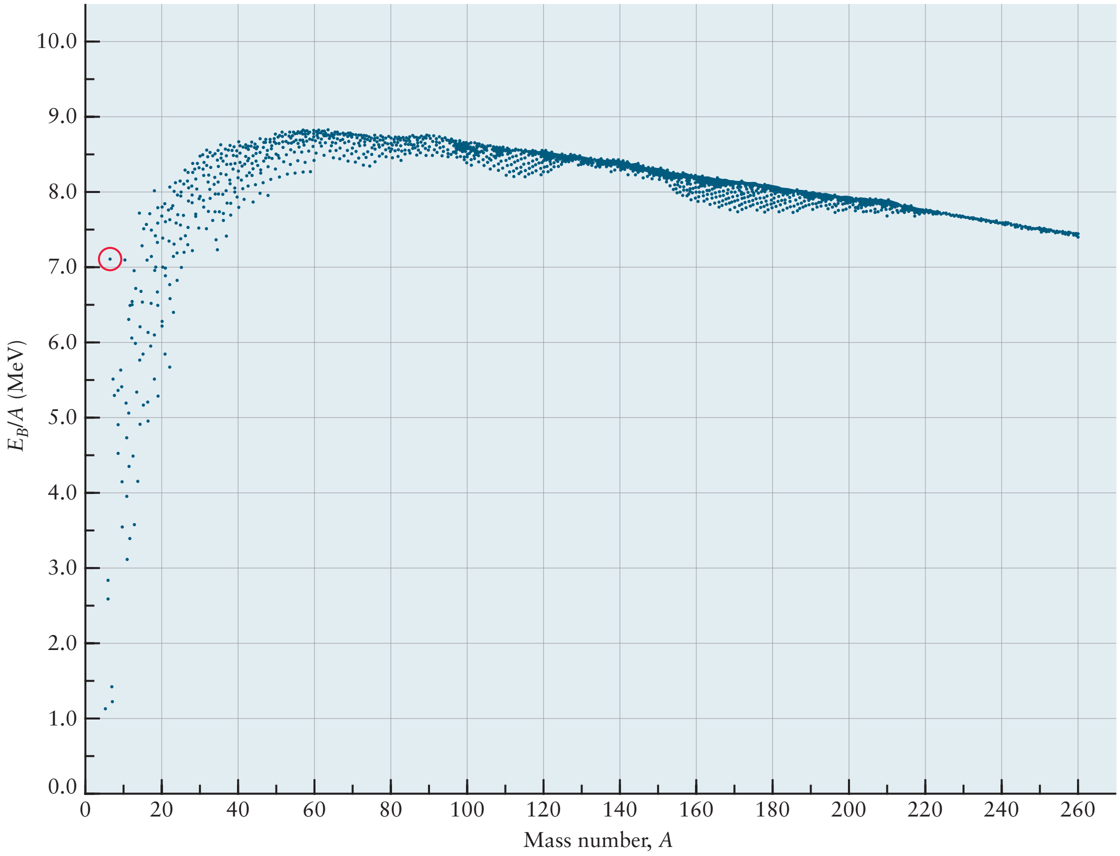

FIGURE 19.2 The variation of the binding energy per nucleon with mass number. A total of 2212 nuclides are shown, of which 274 are stable. The greatest nuclear stability is seen in the vicinity of ${}^{56}\mathrm{Fe}$. Note that ${}^{4}\mathrm{He}$ (red circle) is unusually stable for its mass number.

the free energy change is essentially equal to it, and the thermodynamic criterion for spontaneous nuclear reaction consequently simplifies to

$$\Delta E < 0 \qquad \text{or} \qquad \Delta m < 0$$

The equivalence of these criteria follows from Einstein's mass–energy relationship. Spontaneous transformations of one nucleus into others can occur only if the combined mass of products is less than the mass of the original nuclide.

Before we address the details of nuclear decay, it is necessary to mention **antiparticles**. Each subatomic particle is thought to have an antiparticle of the same mass but opposite charge. Thus, the antiparticle of an electron is a **positron** (e^+), and the antiparticle of a proton is a negatively charged particle called an **antiproton.** Antiparticles have only transient existences because matter and antimatter annihilate one another when they come together, emitting radiation carrying an equivalent amount of energy. In the case of an electron and a positron, two oppositely directed **gamma rays** (γ-rays; high-energy photons), called the **annihilation radiation,** are emitted. Another important particle–antiparticle pair is the neutrino (symbol ν) and antineutrino ($\tilde{\nu}$), both of which are uncharged and almost massless. (They differ only in parity, a quantum-mechanical symmetry upon reflection.) Neutrinos interact so weakly with matter that elaborate detectors are required to record the extremely rare events induced by them in selected nuclides.

Beta Decay

If an unstable nuclide contains fewer protons than do stable isotopes of the same mass number, it is called "proton deficient." Such a nucleus can decay by transforming one of its neutrons into a proton and emitting a high-energy electron ${}_{-1}^{0}e^-$, also called a **beta particle,** and an antineutrino ($\tilde{\nu}$). The superscript 0 indicates a mass number of 0 because an electron contains neither protons nor neutrons and has a much smaller mass than a nucleus. The subscript -1 indicates the negative charge on the particle. It is not a true "atomic number," but writing the symbol in this way is helpful in balancing nuclear equations. The nuclide that results has the same mass number A, but its atomic number Z is increased by 1 because a neutron has been transformed into a proton. Examples of **beta decay** of unstable nuclei are

$$ {}_{6}^{14}\mathrm{C} \longrightarrow {}_{7}^{14}\mathrm{N} + {}_{-1}^{0}e^- + \tilde{\nu} \qquad {}_{11}^{24}\mathrm{Na} \longrightarrow {}_{12}^{24}\mathrm{Mg} + {}_{-1}^{0}e^- + \tilde{\nu} $$

The criterion $\Delta m < 0$ for spontaneous beta decay requires that

$$\underset{\text{(Parent nucleus)}}{m[{}^{A}Z]} > \underset{\text{(Daughter nucleus)}}{m[{}^{A}(Z+1)]} + m[{}_{-1}^{0}e^-]$$

because the mass of the antineutrino ($\tilde{\nu}$) is almost zero. This inequality refers to the masses of the parent and daughter *nuclei* and the emitted electron. It must be reformulated in terms of neutral *atom* masses because the mass spectrometer yields masses of atoms rather than nuclei. To do this, add the mass of Z electrons to both sides, giving a total of $Z + 1$ electrons on the right side (because the emitted ${}_{-1}^{0}e^-$ is also counted). The inequality becomes

$$\underset{\text{(Parent atom)}}{m[{}^{A}Z]} > \underset{\text{(Daughter atom)}}{m[{}^{A}(Z+1)]}$$

A direct comparison of atomic masses (Table 19.1) lets us determine whether beta emission can take place.

The condition that energy be released follows from the Einstein mass–energy relation:

$$\Delta E = c^2\{m[{}^{A}(Z+1)] - m[{}^{A}Z]\} < 0$$

The liberated energy is carried off as kinetic energy by the beta particle (electron) and the antineutrino, because the nucleus produced is heavy enough that its recoil energy is small and can be neglected. The kinetic energy of the electron can fall anywhere in a continuous range from 0 up to $-\Delta E$ (Fig. 19.3), with the antineutrino carrying off the balance of the energy.

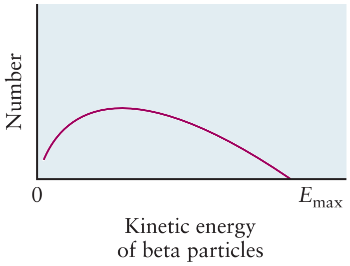

FIGURE 19.3 Emitted beta particles have a distribution of kinetic energies up to a cutoff value of E_{max}.

EXAMPLE 19.2

Calculate the maximum kinetic energy of the electron in the decay

$$^{14}_{6}\text{C} \longrightarrow {}^{14}_{7}\text{N} + {}^{\ 0}_{-1}e^{-} + \tilde{\nu}$$

SOLUTION

Table 19.1 gives the masses of the relevant atoms. From them we calculate

$$\Delta m = m[^{14}_{7}\text{N}] - m[^{14}_{6}\text{C}] = 14.0030740 - 14.0032420 = -0.0001680 \text{ u}$$

$$\Delta E = (-1.68 \times 10^{-4} \text{ u})(931.5 \text{ MeV u}^{-1}) = -0.156 \text{ MeV}$$

The maximum kinetic energy of the electron is 0.156 MeV.

Related Problem: 8

Positron Emission

When a nucleus has too many protons for stability relative to the number of neutrons it contains, it may decay by emitting a positron. In this event a proton is converted to a neutron, and a high-energy positron (symbolized ${}^{0}_{1}e^{+}$) and a neutrino (ν) are emitted. As in beta decay, the mass number of the nuclide remains the same, but now the atomic number Z *decreases* by 1. Examples of **positron emission** are

$$^{11}_{6}\text{C} \longrightarrow {}^{11}_{5}\text{B} + {}^{0}_{1}e^{+} + \nu \qquad {}^{19}_{10}\text{Ne} \longrightarrow {}^{19}_{9}\text{F} + {}^{0}_{1}e^{+} + \nu$$

The positron has the same mass as an electron but has a positive charge. The mass criterion $\Delta m < 0$ is different from that for beta decay. For the bare nuclei the criterion is

$$\underset{\text{(Parent nucleus)}}{m[^{A}Z]} > \underset{\text{(Daughter nucleus)}}{m[^{A}(Z-1)]} + m[^{0}_{1}e^{+}]$$

Adding the mass of Z electrons to both sides gives the mass of the neutral atom ^{A}Z on the left, but only $Z - 1$ electrons are needed on the right side to form a neutral atom $^{A}(Z - 1)$. This leaves additional electron and positron masses on the right. These masses are the same, so the criterion for spontaneous positron emission is

$$\underset{\text{(Parent atom)}}{m[^{A}Z]} > \underset{\text{(Daughter atom)}}{m[^{A}(Z-1)]} + 2m[^{0}_{1}e^{+}]$$

The energy change in positron emission is

$$\Delta E = c^2\{m[^{A}(Z-1)] + 2m[^{0}_{1}e^{+}] - m[^{A}Z]\} < 0$$

The kinetic energy ($-\Delta E$) is distributed between the positron and the neutrino.

EXAMPLE 19.3

Calculate the maximum kinetic energy of the positron emitted in the decay

$$^{11}_{6}\text{C} \longrightarrow {}^{11}_{5}\text{B} + {}^{0}_{1}e^{+} + \nu$$

SOLUTION

The change in mass is

$$\Delta m = m[{}^{11}_{5}\text{B}] + 2m[{}^{0}_{1}e^{+}] - m[{}^{11}_{6}\text{C}] = 11.0093055 + 2(0.00054858) - 11.011433$$

$$= -0.00130 \text{ u}$$

The energy change is then

$$\Delta E = (-0.00130 \text{ u})(931.5 \text{ MeV u}^{-1}) = -0.960 \text{ MeV}$$

The maximum kinetic energy of the positron is +0.960 MeV.

Related Problem: 7

Electron Capture

If $m[{}^{A}Z]$ exceeds $m[{}^{A}(Z-1)]$ (both referring to neutral atoms) but by less than 1.0972×10^{-3} u (equivalent to $2m[{}^{0}_{1}e^{+}]$), positron emission cannot occur. An alternative process that *is* allowed is **electron capture,** in which an electron outside the nucleus of the parent atom is captured by the nucleus and a proton is converted to a neutron. As in positron emission, the mass number is unchanged and the atomic number decreases by 1. In this case, however, the only particle emitted is a neutrino. An example is

$${}^{231}_{92}\text{U} + {}^{0}_{-1}e^{-} \longrightarrow {}^{231}_{91}\text{Pa} + \nu$$

The mass criterion for electron capture is simply that

$$\underset{\text{(Parent atom)}}{m[{}^{A}Z]} > \underset{\text{(Daughter atom)}}{m[{}^{A}(Z-1)]}$$

so the energy change is

$$\Delta E = c^{2}\{m[{}^{A}(Z-1)] - m[{}^{A}Z]\} < 0$$

Electron capture is common for heavier neutron-deficient nuclei, for which the mass change with atomic number is too small for positron emission to be possible. In the preceding example,

$$\Delta m = m[{}^{231}_{91}\text{Pa}] - m[{}^{231}_{92}\text{U}] = 231.035879 - 231.03689 = 0.00041 \text{ u}$$

Because $\Delta m < 0$, this process can and does occur by electron capture, but because 0.00041 u is less than $2m[{}^{0}_{1}e^{+}]$, the analogous process could not occur through positron emission.

Alpha Decay

The three forms of decay discussed so far all lead to changes in the atomic number Z but not in the mass number A. Another process, **alpha decay,** involves the emission of an alpha particle (${}^{4}_{2}\text{He}^{2+}$ ion) and a decrease in mass number A by 4 (the atomic number Z and the neutron number N each decrease by 2). An example is

$${}^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$$

Such alpha decay occurs chiefly for elements in the unstable region beyond bismuth ($Z = 83$) in the periodic table.

The criterion for alpha decay is once again $\Delta m < 0$. In the preceding example,

$$\Delta m = \underset{\text{(Atom)}}{m[{}^{234}_{90}\text{Th}]} + \underset{\text{(Atom)}}{m[{}^{4}_{2}\text{He}]} - \underset{\text{(Atom)}}{m[{}^{238}_{92}\text{U}]}$$

$$= 234.043595 + 4.002603 - 238.050783 \text{ u} = -0.004585 \text{ u} < 0$$

$$\Delta E = (-0.004585 \text{ u})(931.5 \text{ MeV u}^{-1}) = -4.27 \text{ MeV}$$

Most of the energy is carried away by the lighter helium atom, with a small fraction appearing as recoil energy of the heavy thorium atom.

Other Modes of Decay

The arrows in Figure 19.1 show the directions of the types of decay discussed so far. Nuclei whose values of N/Z are too great move toward the line of stability by beta emission, whereas those whose values are too small undergo positron emission or electron capture. Nuclei that are simply too massive can move to lower values of both N and Z by alpha emission. The range of stable nuclides is limited by the interplay of attractive nuclear forces and repulsive Coulomb forces between protons in the nucleus. Scientists believe that it is unlikely that additional stable elements will be found, although long-lived radioactive nuclides may well exist at still higher Z.

When nuclei are very proton-deficient or very neutron-deficient, an excess particle may "boil off," that is, be ejected directly from the nucleus. These decay modes are called **neutron emission** and **proton emission,** respectively, and move nuclides down or to the left in Figure 19.1. Finally, certain unstable nuclei undergo spontaneous **fission,** in which they split into two nuclei of roughly equal size. Nuclear fission will be discussed in more detail in Section 19.5.

Detecting and Measuring Radioactivity

Many methods have been developed to detect, identify, and quantitatively measure the products of nuclear reactions. Some are quite simple, but others require complex electronic instrumentation. Perhaps the simplest radiation detector is the **photographic emulsion,** first used by Henri Becquerel, the discoverer of radioactivity. In 1896 Becquerel reported his observation that potassium uranyl sulfate ($K_2UO_2(SO_4)_2 \cdot 2H_2O$) could expose a photographic plate even in the dark. Such detectors are still used today in the film badges that are worn to monitor exposure to penetrating radiation. The degree of darkening of the film is proportional to the quantity of radiation received.

Rutherford and his students used a screen coated with zinc sulfide to detect the arrival of alpha particles by the pinpoint scintillations of light they produce. That simple device has been developed into the modern **scintillation counter.** Instead of a ZnS screen, the modern scintillation counter uses a crystal of sodium iodide, in which a small fraction of the Na^+ ions have been replaced by thallium (Tl^+) ions. The crystal emits a pulse of light when it absorbs a beta particle or a gamma ray, and a photomultiplier tube detects and counts the light pulses.

The **Geiger counter** (Fig. 19.4) consists of a cylindrical tube, usually of glass, coated internally with metal to provide a negative electrode and with a wire down the center for a positive electrode. The tube is filled to a total pressure of about 0.1 atm with a mixture of 90% argon and 10% ethyl alcohol vapor, and a potential difference of about 1000 V is applied across the electrodes. When a high-energy electron (beta particle) enters the tube, it produces positive ions and electrons. The light electrons are quickly accelerated toward the positively

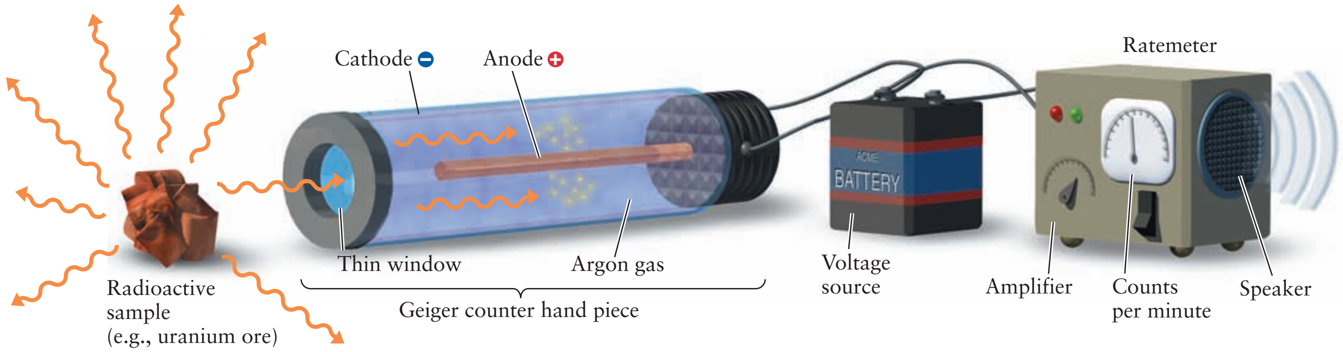

FIGURE 19.4 In a Geiger tube, radiation ionizes gas in the tube, freeing electrons that are accelerated to the anode wire in a cascade. Their arrival creates an electrical pulse, which is detected by a ratemeter. The ratemeter displays the accumulated pulses as the number of ionization events per minute.

charged wire. As they advance, they encounter and ionize other neutral atoms. An avalanche of electrons builds up, and a large electron current flows into the central wire. This causes a drop in the potential difference, which is recorded, and the multiplicative electron discharge is quenched by the alcohol molecules. In this way single beta particles produce electrical pulses that can be amplified and counted. Portable Geiger counters are widely used in uranium prospecting and to measure radiation in workplaces.

19.3 Kinetics of Radioactive Decay

The decay of any given unstable nucleus is a random event and is independent of the number of surrounding nuclei that have decayed. When the number of nuclei is large, we can be confident that during any given period a definite fraction of the original number of nuclei will have undergone a transformation into another nuclear species. In other words, the rate of decay of a collection of nuclei is proportional to the number of nuclei present, showing that nuclear decay follows a first-order rate equation of the type discussed in Chapter 18. All the results developed in that chapter apply to the present situation; for example, the integrated rate law has the form

$$N = N_i e^{-kt}$$

where N_i is the number of nuclei originally present at $t = 0$. The decay constant k is related to a half-life $t_{1/2}$ through

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k}$$

just as in the first-order gas-phase chemical kinetics of Section 18.2. The half-life is the time required for the nuclei in a sample to decay to one-half their initial number, and it can range from less than 10^{-21} s to more than 10^{24} years for unstable nuclei. Table 19.2 lists the half-lives and decay modes of some unstable nuclides.

There is one important practical difference between chemical kinetics and nuclear kinetics. In chemical kinetics the concentration of a reactant or product is monitored over time, and the rate of a reaction is then found from the rate of change of that concentration. In nuclear kinetics the rate of occurrence of decay events, $-dN/dt$, is measured directly with a Geiger counter or other radiation detector. This decay rate—the average disintegration rate in numbers of nuclei per unit time—is called the **activity** ***A***.

$$A = -\frac{dN}{dt} = kN \qquad [19.2]$$

Because the activity is proportional to the number of nuclei N, it also decays exponentially with time:

$$A = A_i e^{-kt} \qquad [19.3]$$

A plot of ln A against time t is linear with slope $-k = -(\ln 2)/t_{1/2}$, as Figure 19.5 shows. The activity A is reduced to half its initial value in a time $t_{1/2}$. Once A and k are known, the number of nuclei N at that time can be calculated from

$$N = \frac{A}{k} = \frac{At_{1/2}}{\ln 2} = \frac{At_{1/2}}{0.6931}$$

The S.I. unit of activity is the becquerel (Bq), defined as 1 radioactive disintegration per second. An older and much larger unit of activity is the curie (abbreviated Ci), which is defined as 3.7×10^{10} disintegrations per second. The activity of 1 g of radium is 1 Ci.

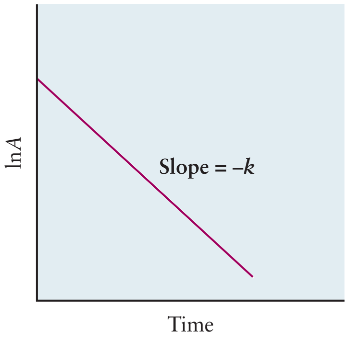

FIGURE 19.5 A graph of the logarithm of the activity of a radioactive nuclide against time is a straight line with slope $-k = -(\ln 2)/t_{1/2}$. The decay rate can also be measured as the ratio of the activity to the number of atoms of the radioisotope, if the latter is known.

TABLE 19.2 Decay Characteristics of Some Radioactive Nuclei

Nuclide	$t_{1/2}$	Decay Mode†	Daughter
$^{3}_{1}\text{H}$ (tritium)	12.26 years	e^-	$^{3}_{2}\text{He}$
$^{8}_{4}\text{Be}$	$\sim 1 \times 10^{-16}$ s	α	$^{4}_{2}\text{He}$
$^{14}_{6}\text{C}$	5730 years	e^-	$^{14}_{7}\text{N}$
$^{22}_{11}\text{Na}$	2.601 years	e^+	$^{22}_{10}\text{Ne}$
$^{24}_{11}\text{Na}$	15.02 hours	e^-	$^{24}_{12}\text{Mg}$
$^{32}_{15}\text{P}$	14.28 days	e^-	$^{32}_{16}\text{S}$
$^{35}_{16}\text{S}$	87.2 days	e^-	$^{35}_{17}\text{Cl}$
$^{36}_{17}\text{Cl}$	3.01×10^{5} years	e^-	$^{36}_{18}\text{Ar}$
$^{40}_{19}\text{K}$	1.28×10^{9} years	e^- (89.3%)	$^{40}_{20}\text{Ca}$
		E.C. (10.7%)	$^{40}_{18}\text{Ar}$
$^{59}_{26}\text{Fe}$	44.6 days	e^-	$^{59}_{27}\text{Co}$
$^{60}_{27}\text{Co}$	5.27 years	e^-	$^{60}_{28}\text{Ni}$
$^{90}_{38}\text{Sr}$	29 years	e^-	$^{90}_{39}\text{Y}$
$^{109}_{48}\text{Cd}$	453 days	E.C.	$^{109}_{47}\text{Ag}$
$^{125}_{53}\text{I}$	59.7 days	E.C.	$^{125}_{52}\text{Te}$
$^{131}_{53}\text{I}$	8.041 days	e^-	$^{131}_{54}\text{Xe}$
$^{127}_{54}\text{Xe}$	36.41 days	E.C.	$^{127}_{53}\text{I}$
$^{137}_{57}\text{La}$	$\sim 6 \times 10^{4}$ years	E.C.	$^{137}_{56}\text{Ba}$
$^{222}_{86}\text{Rn}$	3.824 days	α	$^{218}_{84}\text{Po}$
$^{226}_{88}\text{Ra}$	1600 years	α	$^{222}_{86}\text{Rn}$
$^{232}_{90}\text{Th}$	1.40×10^{10} years	α	$^{228}_{88}\text{Ra}$
$^{235}_{92}\text{U}$	7.04×10^{8} years	α	$^{231}_{90}\text{Th}$
$^{238}_{92}\text{U}$	4.468×10^{9} years	α	$^{234}_{90}\text{Th}$
$^{239}_{93}\text{Np}$	2.350 days	e^-	$^{239}_{94}\text{Pu}$
$^{239}_{94}\text{Pu}$	2.411×10^{4} years	α	$^{235}_{92}\text{U}$

†E.C. stands for electron capture; e^+ for positron emission; e^- for beta emission; α, for alpha emission.

EXAMPLE 19.4

Tritium (^{3}H) decays by beta emission to ^{3}He with a half-life of 12.26 years. A sample of a tritiated compound has an initial activity of 0.833 Bq. Calculate the number N_i of tritium nuclei in the sample initially, the decay constant k, and the activity after 2.50 years.

SOLUTION

Convert the half-life to seconds:

$$t_{1/2} = (12.26\ \text{yr})(60 \times 60 \times 24 \times 365\ \text{s yr}^{-1}) = 3.866 \times 10^{8}\ \text{s}$$

The number of nuclei originally present was

$$\text{N}_\text{i} = \frac{A_\text{i} t_{1/2}}{\ln 2} = \frac{(0.833\ \text{s}^{-1})(3.866 \times 10^{8}\ \text{s})}{0.6931} = 4.65 \times 10^{8}\ {}^{3}\text{H nuclei}$$

The decay constant k is calculated directly from the half-life:

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.6931}{3.866 \times 10^{8}\ \text{s}} = 1.793 \times 10^{-9}\ \text{s}^{-1}$$

To find the activity after 2.50 years, convert this time to seconds (7.884×10^{7} s) and use

$$A = A_\text{i}\, e^{-kt} = (0.833\ \text{Bq}) \exp\left[-(1.793 \times 10^{-9}\ \text{s}^{-1})(7.884 \times 10^{7}\ \text{s})\right] = 0.723\ \text{Bq}$$

Related Problems: 21, 22

Radioactive Dating

The decay of radioactive nuclides with known half-lives enables geochemists to measure the ages of rocks from their isotopic compositions. Suppose that a uranium-bearing mineral was deposited some 2 billion (2.00×10^9) years ago and has remained geologically unaltered to the present time. The ^{238}U in the mineral decays with a half-life of 4.51×10^9 years to form a series of short-lived intermediates, ending in the stable lead isotope ^{206}Pb (Fig. 19.6). The fraction of uranium remaining after 2.00×10^9 years should be

$$\frac{N}{N_i} = e^{-kt} = e^{-0.6931\ t/t_{1/2}} = \exp\left(\frac{-0.6931 \times 2.00 \times 10^9\ \text{yr}}{4.51 \times 10^9\ \text{yr}}\right) = 0.735$$

and the number of ^{206}Pb atoms should be approximately

$$(1 - 0.735)N_i = 0.265\ N_i(^{238}\text{U})$$

The ratio of abundances

$$\frac{N(^{206}\text{Pb})}{N(^{238}\text{U})} = \frac{0.265}{0.735} = 0.361$$

therefore is determined by the time elapsed since the deposit was originally formed—in this case, 2.00×10^9 years. Of course, to calculate the age of the mineral, we work backward from the measured $N(^{206}\text{Pb})/N(^{238}\text{U})$ ratio.

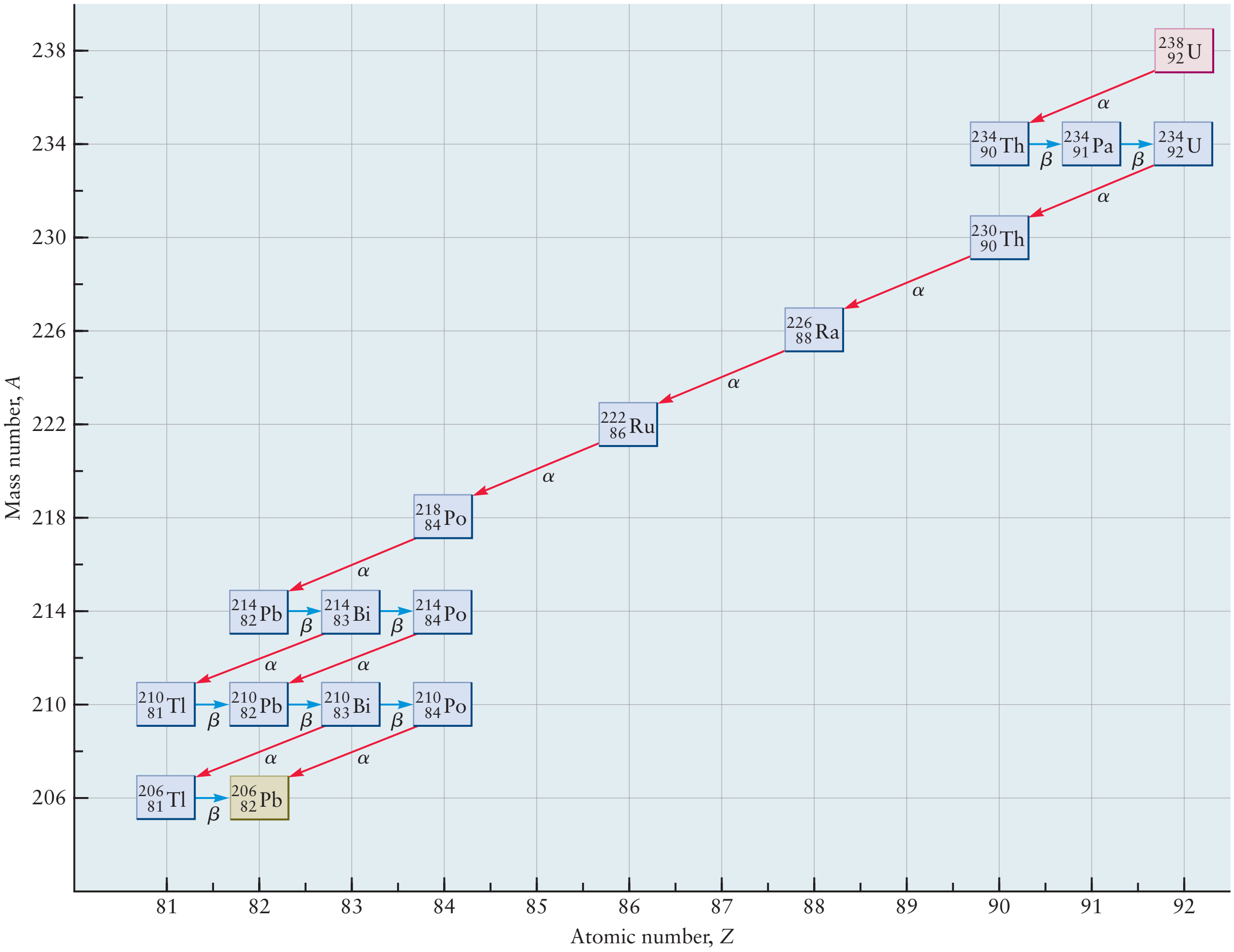

FIGURE 19.6 The radioactive nuclide ^{238}U decays via a series of alpha and beta emissions to the stable nuclide ^{206}Pb.

To use the method, it is necessary to be certain that the stable nuclide generated (^{206}Pb in this case) arises only from the parent species (^{238}U here) and that neither lead nor uranium has left or entered the rock over the course of geologic time. If possible, it is desirable to measure the ratios of several different isotopically paired species in the same rock sample. For example, ^{87}Rb decays to ^{87}Sr with a half-life of 4.9×10^{10} years, and one mode of ^{40}K decay (with a half-life of 1.28×10^{9} years) is to ^{40}Ar. Each pair should ideally yield the same age. Detailed analysis of a large number of samples suggests that the oldest surface rocks on earth are about 3.8 billion years old. An estimate of 4.5 billion years for the age of the earth and solar system comes from indirect evidence involving an isotopic analysis of meteorites, which are believed to have formed at the same time.

A somewhat different type of dating uses measurements of ^{14}C decay, which covers the range of human history and prehistory back to about 30,000 years ago. This unstable species (with a half-life of 5730 years) is produced continuously in the atmosphere. Cosmic rays of very high energy cause nuclear reactions that produce neutrons. These can collide with $^{14}_{7}$N nuclei to produce $^{14}_{6}$C by the reaction

$$^{14}_{7}\text{N} + {}^{1}_{0}n \longrightarrow {}^{14}_{6}\text{C} + {}^{1}_{1}\text{H}$$

The resulting ^{14}C enters the carbon reservoir on the Earth's surface, mixing with stable ^{12}C as dissolved $H^{14}CO_3^-$ in the oceans, as $^{14}CO_2$ in the atmosphere, and in the tissues of plants and animals. This mixing, which is believed to have occurred at a fairly constant rate over the past 50,000 years, means that the ^{14}C in a living organism has a specific activity of close to 15.3 disintegrations per minute per gram of total carbon—that is, 0.255 Bq g^{-1}. When a plant or animal dies (for example, when a tree is cut down), the exchange of carbon with the surroundings stops and the amount of ^{14}C in the sample falls exponentially with time. By measuring the ^{14}C activity remaining in an archaeological sample, we can estimate its age. This ^{14}C dating method, developed by the American chemist W. F. Libby, has been calibrated against other dating techniques (such as counting the annual rings of bristlecone pines or examining the written records that may accompany a carbon-containing artifact) and has been found to be quite reliable over the time span for which it can be checked. This indicates an approximately constant rate of production of ^{14}C near the earth's surface over thousands of years. Burning fossil fuels has decreased the isotopic abundance of $^{14}CO_2$ in the atmosphere because plants (the source of fossil fuels) preferentially use $^{12}CO_2$ in photosynthesis. The changing isotopic composition of atmospheric CO_2 will cause difficulty in applying ^{14}C dating in the future.

EXAMPLE 19.5

A wooden implement has a specific activity of ^{14}C of 0.195 Bq g^{-1}. Estimate the age of the implement.

SOLUTION

The decay constant for ^{14}C is

$$k = \frac{0.6931}{5730\ \text{yr}} = 1.21 \times 10^{-4}\ \text{yr}^{-1}$$

The initial specific activity was 0.255 Bq g^{-1}, and the measured activity now (after t years) is 0.195 Bq g^{-1}, so

$$A = A_i e^{-kt}$$

$$0.195\ \text{Bq g}^{-1} = 0.255\ \text{Bq g}^{-1} e^{-(1.21 \times 10^{-4})t}$$

$$\ln\left(\frac{0.195}{0.255}\right) = -(1.21 \times 10^{-4}\ \text{yr}^{-1})t$$

$$t = 2200\ \text{yr}$$

The implement comes from a tree cut down approximately 2200 years ago.

Related Problems: 25, 26

19.4 Radiation in Biology and Medicine

Radiation has both harmful and beneficial effects for living organisms. All forms of radiation cause damage in direct proportion to the amount of energy they deposit in cells and tissues. The damage takes the form of chemical changes in cellular molecules, which alter their functions and lead either to uncontrolled multiplication and growth of cells or to their death. Alpha particles lose their kinetic energy over very short distances in matter (typically 10 cm in air or 0.05 cm in water or tissues), producing intense ionization in their wakes until they accept electrons and are neutralized to harmless helium atoms. Radium, for example, is an alpha emitter that substitutes for calcium in bone tissue and destroys its capacity to produce both red and white blood cells. Beta particles, gamma rays, and x-rays have greater penetrating power than alpha particles and so present a radiation hazard even when their source is well outside an organism.

The amount of damage produced in tissue by any of these kinds of radiation is proportional to the number of particles or photons and to their energy. A given activity of tritium causes less damage than the same activity of ^{14}C, because the beta particles from tritium have a maximum kinetic energy of 0.0179 MeV, whereas those from ^{14}C have an energy of 0.156 MeV. What is important is the amount of ionization produced or the quantity of energy deposited by radiation. For this purpose, several units are used. The *rad* (*r*adiation *a*bsorbed *d*ose) is defined as the amount of radiation that deposits 10^{-2} J of energy per kilogram of tissue. The damage produced in human tissue depends on still other factors, such as the nature of the tissue, the kind of radiation, the total radiation dose, and the dose rate. To take all these into account, the *rem* (*r*oentgen *e*quivalent in *m*an) has been defined to measure the effective dosages of radiation received by humans. A physical dose of 1 rad of beta or gamma radiation translates into a human dose of 1 rem. Alpha radiation is more toxic; a physical dose of 1 rad of alpha radiation equals about 10 rems. The SI unit for absorbed radiation, analogous to the rad, is the gray (Gy); 1 Gy = 1 joule per kg of material. So, 1 Gy = 100 rad. The SI unit for effective dosage of radiation is the sievert (Sv). The sievert is defined in the same way as the rem, except the delivered dose is expressed in Gy instead of rad; consequently, 1 Sv = 100 rem.

Exposure to radiation is unavoidable. The average person in the United States receives about 100 millirems (mrem) or 1 millisievert (mSv) annually from natural sources that include cosmic radiation and radioactive nuclides such as ^{40}K and ^{222}Rn. Another 50 to 100 mrem or 0.5 to 1.0 mSv (variable) comes from human activities (including dental and medical x-ray examinations and airplane flights, which increase exposure to cosmic rays higher in the atmosphere). The safe level of exposure to radiation is a controversial issue among biologists; one group maintains that the effects of radiation are cumulative, another that a threshold dose is necessary for pathological change. The problem is made even more complex by the necessity to distinguish between tissue damage in an exposed individual and genetic damage, which may not become apparent for several generations. It is much easier to define the radiation level that, with high probability, will cause death in an exposed person. The LD_{50} level in human beings (the level carrying a 50% probability that death will result within 30 days after a single exposure) is 500 rad, or 5 Gy.

EXAMPLE 19.6

The beta decay of ^{40}K that is a natural part of the body makes all human beings slightly radioactive. An adult weighing 70.0 kg contains about 170 g of potassium. The relative natural abundance of ^{40}K is 0.0118%, its half-life is 1.28×10^9 years, and its beta particles have an average kinetic energy of 0.55 MeV.

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FIGURE 19.7 A medical physicist unloading ^{99m}Tc from an Amertec II generator in preparation for gamma scintigraphy (gamma camera scanning). ^{99m}Tc is an excited state of ^{99}Tc that decays to the nuclear ground state by emission of gamma rays. This isotope is used in nuclear medicine to study the heart. The ^{99m}Tc is taken up by heart tissue; a gamma-ray detector then provides an image of the heart.

(a) Calculate the total activity of ^{40}K in this person.

(b) Determine (in Gy per year) the annual radiation absorbed dose arising from this internal ^{40}K.

SOLUTION

(a) First calculate the decay constant of ^{40}K in s^{-1}:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{(1.28 \times 10^{9}\ \text{yr})(365 \times 24 \times 60 \times 60\ \text{s yr}^{-1})}$$

$$= 1.72 \times 10^{-17}\ \text{s}^{-1}$$

$$\text{number of } ^{40}\text{K atoms} = \frac{170\ \text{g}}{40.0\ \text{g mol}^{-1}}(1.18 \times 10^{-4})(6.02 \times 10^{23}\ \text{mol}^{-1})$$

$$= 3.02 \times 10^{20}$$

$$A = -\frac{dN}{dt} = kN = (1.72 \times 10^{-17}\ \text{s}^{-1})(3.02 \times 10^{20}) = 5.19 \times 10^{3}\ \text{s}^{-1}$$

(b) Each disintegration of ^{40}K emits an average of 0.55 MeV of energy, and we assume that all of this energy is deposited within the body. From part (a), 5.19×10^{3} disintegrations occur per second, and we know how many seconds are in a year. The total energy deposited per year is then

$$5.19 \times 10^{3}\ \text{s}^{-1} \times (60 \times 60 \times 24 \times 365\ \text{s yr}^{-1}) \times 0.55\ \text{MeV} = 9.0 \times 10^{10}\ \text{MeV yr}^{-1}$$

Next, because a Gy is 1 J per kilogram of tissue, we express this answer in joules per year:

$$(9.0 \times 10^{10}\ \text{MeV yr}^{-1})(1.602 \times 10^{-13}\ \text{J MeV}^{-1}) = 0.0144\ \text{J yr}^{-1}$$

Each kilogram of body tissue receives 1/70.0 of this amount of energy per year, because the person weighs 70.0 kg. The dose is thus 21×10^{-5} J kg^{-1} yr^{-1}, which is equivalent to 0.21 Gy yr^{-1} or 21 mrad yr^{-1}. This is about a fifth of the annual background dosage received by a person.

Related Problems: 35, 36

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FIGURE 19.8 A patient undergoing a PET brain scan, as seen from the radiographer's control room.

Although radiation can do great harm, it confers great benefits in medical applications (Fig. 19.7). The diagnostic importance of x-ray imaging hardly needs mention. Both x-rays and gamma rays are used selectively in cancer therapy to destroy malignant cells. The beta-emitting ^{131}I nuclide finds use in the treatment of cancer of the thyroid because iodine is taken up preferentially by the thyroid gland. Heart pacemakers use the decay of tiny amounts of radioactive ^{238}Pu, converted to electrical energy.

Positron emission tomography (PET) is an important diagnostic technique using radiation (Fig.19.8). It employs radioisotopes such as ^{11}C (half-life 20.3 min) or ^{15}O (half-life 124 s) that emit positrons when they decay. These are incorporated (quickly, because of their short half-lives) into substances such as glucose, which are injected into the patient. By following the pattern of positron emission from the body, researchers can study blood flow and glucose metabolism in healthy and diseased individuals. Computer-reconstructed pictures of positron emissions from the brain are particularly useful, because the locations of glucose metabolism appear to differ between healthy persons and patients with ailments such as manic depression (bipolar disorder) and schizophrenia.

Less direct benefits come from other applications. An example is the study of the mechanism of photosynthesis, in which carbon dioxide and water are combined to form glucose in the green leaves of plants.

$$6\ \text{CO}_2(g) + 6\ \text{H}_2\text{O}(\ell) \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\ \text{O}_2(g)$$

Exposure of plants to CO_2 containing a higher-than-normal proportion of ^{14}C as a tracer enables scientists to follow the mechanism of the reaction. The plants are analyzed at intervals to find what compounds contain ^{14}C in their molecules and thereby to identify the intermediates in photosynthesis. Radioactive tracers are also widely used in medical diagnosis. The radioimmunoassay technique, invented by Nobel laureate Rosalind Yalow, determines the levels of drugs and hormones in body fluids.

19.5 Nuclear Fission

The nuclear reactions considered so far have been spontaneous, first-order decays of unstable nuclides. By the 1920s, physicists and chemists were using particle accelerators to bombard samples with high-energy particles to *induce* nuclear reactions. One of the first results of this program was the identification in 1932 by the English physicist James Chadwick (a student of Rutherford) of the neutron as a product of the reaction of alpha particles with light nuclides such as ^{9}Be:

$$^{4}_{2}He + ^{9}_{4}Be \longrightarrow ^{1}_{0}n + ^{12}_{6}C$$

Shortly after Chadwick's discovery, a group of physicists in Rome, led by Enrico Fermi, began to study the interaction of neutrons with the nuclei of various elements. The experiments produced a number of radioactive species, and it was evident that the absorption of a neutron increased the $N:Z$ ratio in target nuclei above the stability line (see Fig. 19.1). One of the targets used was uranium, the heaviest naturally occurring element. Several radioactive products resulted, none of which had chemical properties characteristic of the elements between $Z = 86$ (radon) and $Z = 92$ (uranium). It appeared to the Italian scientists in 1934 that several new transuranic elements ($Z > 92$) had been synthesized, and an active period of investigation followed.

In 1938 in Berlin, Otto Hahn and Fritz Strassmann sought to characterize the supposed transuranic elements. To their bewilderment, they found instead that barium ($Z = 56$) appeared among the products of the bombardment of uranium by neutrons. Hahn informed his former colleague Lise Meitner, and she conjectured that the products of the bombardment of uranium by neutrons were not transuranic elements but fragments of uranium atoms resulting from a process she termed **fission**. The implication of this phenomenon—the possible release of enormous amounts of energy—was immediately evident. When the outbreak of World War II appeared imminent in the summer of 1939, Albert Einstein wrote to President Franklin Roosevelt to inform him of the possible military uses of fission and of his concern that Germany might develop a nuclear explosive. As a result, in 1942 President Roosevelt authorized the Manhattan District Project, an intense, coordinated effort by a large number of physicists, chemists, and engineers to make a fission bomb of unprecedented destructive power.

The operation of the first atomic bomb hinged on the fission of uranium in a chain reaction induced by absorption of neutrons. The two most abundant isotopes of uranium are ^{235}U and ^{238}U, whose natural relative abundances are 0.720% and 99.275%, respectively. Both undergo fission upon absorbing a neutron, the latter only with "fast" neutrons and the former with both "fast" and "slow" neutrons. In the early days of neutron research, it was not known that the absorption of neutrons by nuclei depends strongly upon neutron velocity. By accident, Fermi and his colleagues discovered that experiments conducted on a wooden table led to a much higher yield of radioactive products than those performed on a marble-topped table. Fermi then repeated the irradiation experiments with a block of paraffin wax interposed between the radium–beryllium neutron source and the target sample, with the startling result that the induced level of radioactivity was greatly enhanced. Within hours Fermi had found the explanation: The high-energy neutrons emitted from the radium–beryllium source were reduced to thermal energy by collision with the low-mass nuclei of the paraffin molecules. Because of their lower energies, their probability of reaction with ^{235}U was greater and a higher yield was achieved. Hydrogen nuclei and the nuclei of other light elements such as ^{12}C (in graphite) are very effective in reducing the energies of high-velocity neutrons and are called **moderators.**

The fission of ^{235}U follows many different patterns, and some 34 elements have been identified among the fission products. In any single fission event two particular nuclides are produced together with two or three secondary neutrons; collectively, they carry away about 200 MeV of kinetic energy. Usually, the daughter nuclei have different *Z* and *A* numbers, so the fission process is asymmetric. Three of the many pathways are

$$
{}^{1}_{0}n + {}^{235}_{92}\text{U} \longrightarrow \begin{cases} {}^{72}_{30}\text{Zn} + {}^{162}_{62}\text{Sm} + 2\,{}^{1}_{0}n \\ {}^{80}_{38}\text{Sr} + {}^{153}_{54}\text{Xe} + 3\,{}^{1}_{0}n \\ {}^{94}_{36}\text{Kr} + {}^{139}_{56}\text{Ba} + 3\,{}^{1}_{0}n \end{cases}
$$

Figure 19.9 shows the distribution of the nuclides produced. The emission of more than one neutron per neutron absorbed in the fission process means that this is a branching chain reaction in which the number of neutrons grows exponentially with time (Fig. 19.10). Permitted to proceed unchecked, this reaction would quickly lead to the release of enormous quantities of energy. Neutrons can be lost by various processes, so it is not obvious that a self-propagating reaction will occur. On December 2, 1942, Fermi and his associates demonstrated that a self-sustaining neutron chain reaction occurred in a uranium "pile" with a graphite moderator. They limited its power output to $\frac{1}{2}$ J s^{-1} by inserting cadmium control rods to absorb neutrons, thereby balancing the rates of neutron generation and loss.

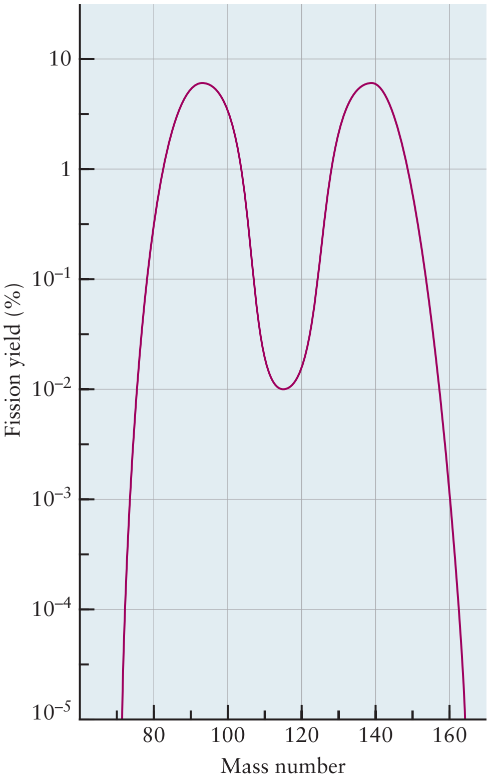


FIGURE 19.9 The distribution of nuclides produced in the fission of ^{235}U has two peaks. Nuclei having mass numbers in the vicinity of $A = 95$ and $A = 139$ are formed with the highest yield; those with $A \approx 117$ are produced with lower probability.

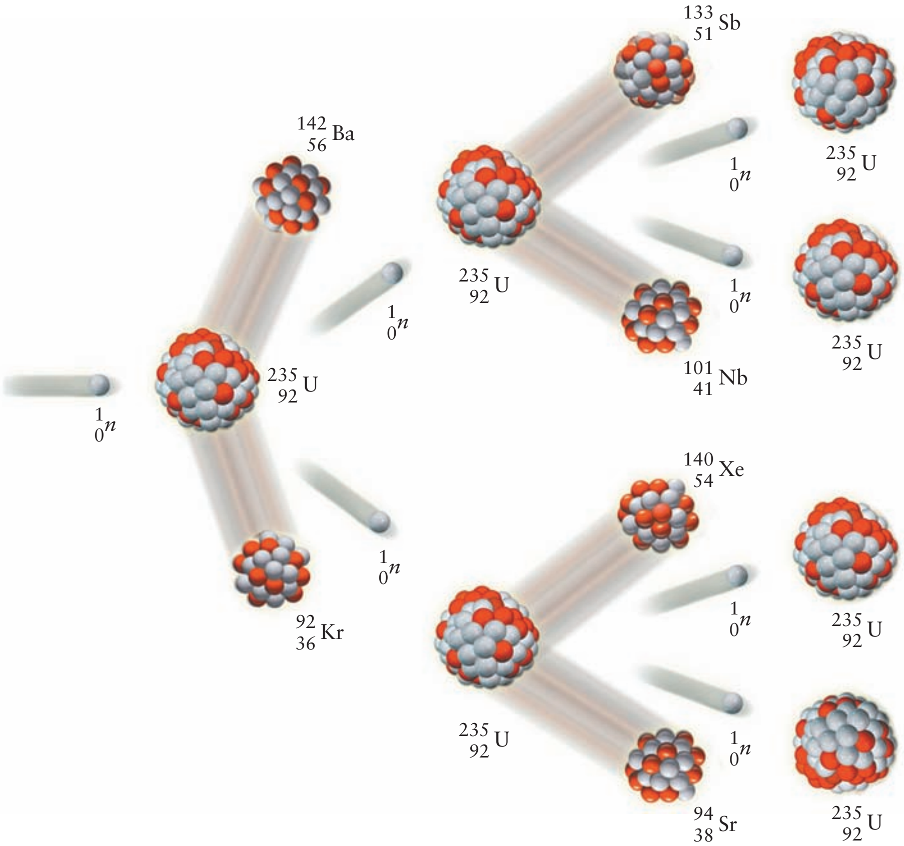


FIGURE 19.10 In a self-propagating nuclear chain reaction, the number of neutrons grows exponentially during fission.

Fermi's work made two developments possible: (1) the exploitation of nuclear fission for the controlled generation of energy in nuclear reactors and (2) the production of ^{239}Pu, a slow- and fast-neutron fissionable isotope of plutonium, as an alternative to ^{235}U for the construction of atomic bombs. For the sudden release of energy required in an explosive, it was necessary to obtain ^{235}U or ^{239}Pu in a state free of neutron-absorbing impurities. Both alternatives were pursued simultaneously. The first required enriching ^{235}U from its relative abundance of 0.72% in natural uranium. This was accomplished through gaseous diffusion (see Section 9.8). For the second alternative, ^{239}Pu was recovered from the partially spent uranium fuel of large nuclear reactors by means of redox reactions, precipitation, and solvent extraction.

Although Fermi and his associates were the first scientists to demonstrate a self-sustaining nuclear chain reaction, a natural uranium fission reactor "went critical" about 1.8 billion years ago in a place now called Oklo, in the Gabon Republic of equatorial Africa. In 1972 French scientists discovered that the ^{235}U content of ore from a site in the open-pit mine at Oklo was only 0.7171%; the normal content of ore from other areas of the mine was 0.7207%. Although this deviation was not large, it was significant, and an investigation revealed that other elements were also present in the ore, in the exact proportions expected after nuclear fission. This discovery established that a self-sustaining nuclear reaction had occurred at Oklo. The geological age of the ore body was found to be about 1.8×10^9 years, and the original ^{235}U concentration is calculated to have been about 3%. From the size of the active ore mass and the depletion of ^{235}U, it is estimated that the reactor generated about 15,000 megawatt-years (5×10^{17} J) of energy over about 100,000 years.

Nuclear Power Reactors

Most **nuclear power reactors** in the United States (Fig. 19.11) use rods of U_3O_8 as fuel. The uranium is primarily ^{238}U, but the amount of ^{235}U is enriched above natural abundance to a level of about 3%. The moderator used to slow the neutrons (to increase the efficiency of the fission) is ordinary water in most cases, so these reactors are called "light-water" reactors. The controlled release of energy by nuclear fission in power reactors demands a delicate balance between neutron generation and neutron loss. As mentioned earlier, this is accomplished by means of steel control rods containing ^{112}Cd or ^{10}B, isotopes that have a very large neutron-capture probability. These rods are automatically inserted into or withdrawn from the fissioning system in response to a change in the neutron flux. As the nuclear reaction proceeds, the moderator (water) is heated and transfers its heat to a steam generator. The steam then goes to turbines that generate electricity (Fig. 19.12).

The power reactors discussed so far rely on the fission of ^{235}U, an isotope in extremely limited supply. An alternative is to convert the much more abundant ^{238}U to fissionable plutonium (^{239}Pu) by neutron bombardment:

$$^{238}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{239}_{93}\text{Np} + {}^{0}_{-1}e^{-} \longrightarrow {}^{239}_{94}\text{Pu} + 2\,{}^{0}_{-1}e^{-}$$

Fissionable ^{233}U can also be made from thorium:

$$^{232}_{90}\text{Th} + {}^{1}_{0}n \longrightarrow {}^{233}_{91}\text{Pa} + {}^{0}_{-1}e^{-} \longrightarrow {}^{233}_{92}\text{U} + 2\,{}^{0}_{-1}e^{-}$$

In a **breeder reactor,** in addition to heat being generated by fission, neutrons are absorbed in a blanket of uranium or thorium. This causes the preceding reactions to occur and generates additional fuel for the reactor to use. An advanced technology for breeder reactors uses liquid sodium instead of water as the coolant, allowing the use of faster neutrons than in water-cooled reactors. The faster neutrons cause more complete consumption of radioactive fuels, increasing efficiency and greatly reducing radioactive waste.

The risks associated with the operation of nuclear reactors are small but not negligible, as the failure of the Three Mile Island reactor in the United States in 1979 and the disaster at Chernobyl in the former Soviet Union in 1987 demonstrated. If a reactor has to be shut down quickly, there is danger of a meltdown, in which the heat from the continuing fission processes melts the uranium fuel. Coolant must be circulated until heat from the decay of short-lived isotopes has

Jonathan Turk

FIGURE 19.11 A nuclear power plant. The large structure on the left is a cooling tower; the containment building is the smaller building on the right with the domed top.

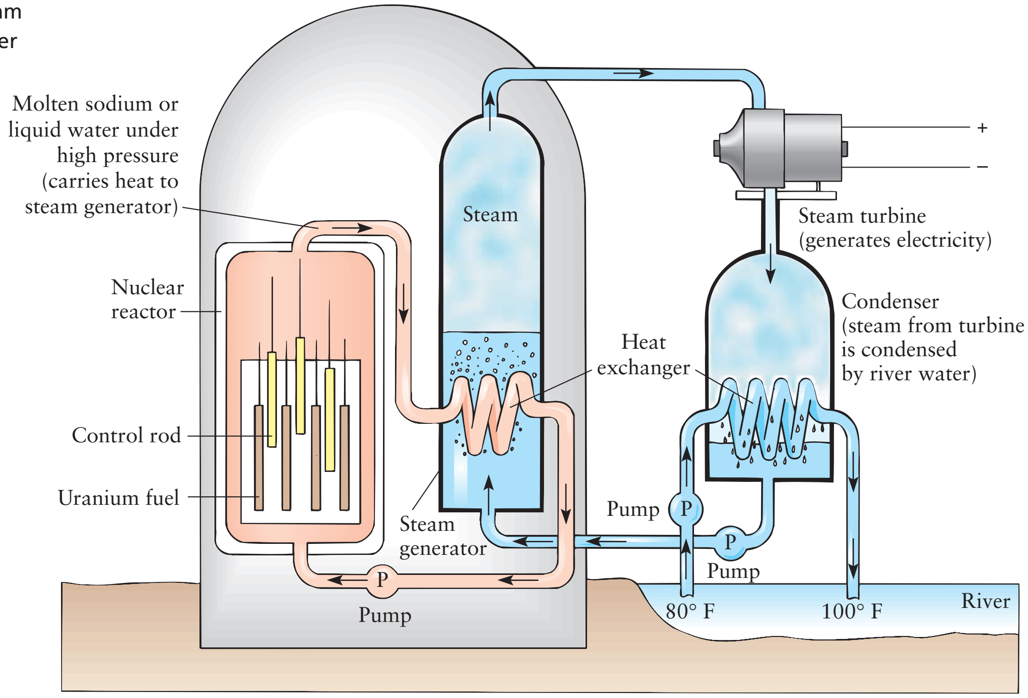


FIGURE 19.12 A schematic diagram of a pressurized-water nuclear power reactor.

been dissipated. The Three Mile Island accident resulted in a partial meltdown because some water coolant pumps were inoperative and others were shut down too soon, causing damage to the core and a slight release of radioactivity into the environment. The Chernobyl disaster was caused by a failure of the water-cooling system and a meltdown. The rapid and uncontrolled nuclear reaction that took place set the graphite moderator on fire and caused the reactor building to rupture, spreading radioactive nuclides with an activity estimated at 2×10^{20} Bq into the atmosphere. A major part of the problem was that the reactor at Chernobyl, unlike those in the United States, was not in a massive containment building.

The safe disposal of the radioactive wastes from nuclear reactors is an important and controversial matter. A variety of proposals have been made, including the burial of radioactive waste in deep mines on either a recoverable or a permanent basis, burial at sea, and launching the waste into outer space. The first alternative is the only one that appears credible. The essential requirement is that the disposal site(s) be stable with respect to possible earthquakes or invasion by underground water. Spent nuclear fuel can be encased in blocks of borosilicate glass, packed in metal containers, and buried in stable rock formations. For a nuclide such as ^{239}Pu, whose half-life is 24,000 years, a storage site that is stable over 240,000 years is needed before the activity drops to 0.1% of its original value. Some shorter lived isotopes are more hazardous over short periods, but their threat diminishes more quickly.

19.6 Nuclear Fusion and Nucleosynthesis

Nuclear fusion is the union of two light nuclides to form a heavier nuclide with the release of energy. Fusion processes are often called **thermonuclear reactions** because they require that the colliding particles possess very high kinetic energies, corresponding to temperatures of millions of degrees, before they are initiated. They are the processes that occur in the sun and other stars. In 1939 the German physicists Hans Bethe (and, independently, Carl von Weizsäcker) proposed that in normal stars (main sequence) the following reactions take place:

$$^{1}_{1}\text{H} + {}^{1}_{1}\text{H} \longrightarrow {}^{2}_{1}\text{H} + {}^{0}_{1}e^{+} + \nu$$

$$^{2}_{1}\text{H} + {}^{1}_{1}\text{H} \longrightarrow {}^{3}_{2}\text{He} + \gamma$$

$$^{3}_{2}\text{He} + {}^{3}_{2}\text{He} \longrightarrow {}^{4}_{2}\text{He} + 2\,{}^{1}_{1}\text{H}$$

In the first reaction, two high-velocity protons fuse to form a deuteron, with the emission of a positron and a neutrino that carry away (as kinetic energy) the additional 0.415 MeV of energy released. In the second reaction, a high-energy deuteron combines with a high-velocity proton to form a helium nucleus of mass 3 and a gamma ray. The third reaction completes the cycle with the formation of a normal helium nucleus ($^{4}_{2}\text{He}$) and the regeneration of two protons. Each of these reactions is exothermic, but up to 1.25 MeV is required to overcome the repulsive barrier between the positively charged nuclei. The overall result of the cycle is to convert hydrogen nuclei to helium nuclei, and the process is called **hydrogen burning.**

As such a star ages and accumulates helium, it begins to contract under the influence of its immense gravity. As it contracts, its helium core heats up; when it reaches a temperature of about 10^8 K, a stage of **helium burning** begins. The first reaction that occurs is

$$2\,{}^{4}_{2}\text{He} \rightleftharpoons {}^{8}_{4}\text{Be}$$

This reaction is written as an equilibrium because the ^{8}Be quickly reverts to helium nuclei with a half-life of only 2×10^{-16} s. Even with this short half-life, the ^{8}Be nuclei are believed to occasionally react with alpha particles to form stable ^{12}C:

$$^{8}_{4}\text{Be} + {}^{4}_{2}\text{He} \longrightarrow {}^{12}_{6}\text{C}$$

The overall effect of the helium-burning phase of a star's life is to convert three helium nuclei to a carbon nucleus, just as helium was formed from four hydrogen nuclei in the hydrogen-burning phase. The density of the core of a star that is burning helium is on the order of 10^5 g cm^{-3}.

This process of **nucleosynthesis** continues beyond the formation of ^{12}C to produce ^{13}N, ^{13}C, ^{14}N, ^{15}O, ^{15}N, and ^{16}O. The stars in this stage are classified as red giants. Similar cycles occur until the temperature of a star core is about 4×10^9 K, its density is about 3×10^6 g cm^{-3}, and the nuclei are ^{56}Fe, ^{59}Co, and ^{60}Ni. These are the nuclei that have the maximum binding energy per nucleon (see Fig. 19.2). It is thought that the synthesis of still heavier nuclei occurs in the immense explosions of supernovae.

Heavy elements can also be produced in particle accelerators, which accelerate ions to high speeds, causing collisions that generate the new elements. Technetium, for example, is not found in nature but was first produced in 1937 when high-energy deuterons were directed at a molybdenum source:

$$^{96}_{42}\text{Mo} + {}^{2}_{1}\text{H} \longrightarrow {}^{97}_{43}\text{Tc} + {}^{1}_{0}n$$

The first **transuranic element** was produced in 1940. Neptunium ($Z = 93$) results from the capture of a neutron by ^{238}U, followed by beta decay. Subsequent work by the American chemist Glenn Seaborg and others led to the production of plutonium ($Z = 94$) and heavier elements. In recent years, nuclides with Z as high as 116 have been made, but in tiny quantities. These nuclides have very short half-lives.

Major efforts are now under way to achieve controlled nuclear fusion as a source of energy. One approach is based on the reaction between deuterium and tritium atoms,

$$^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + {}^{1}_{0}n$$

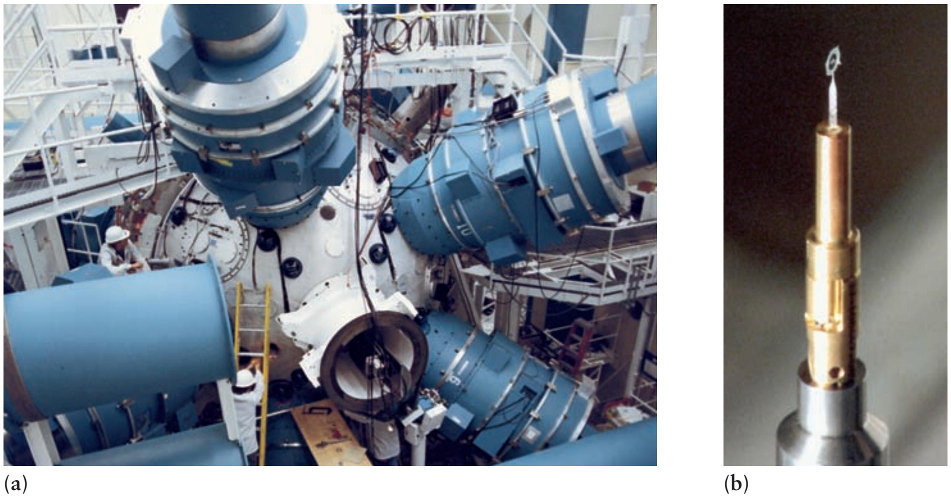


FIGURE 19.13 (a) The target chamber of Nova, a 16-foot-diameter aluminum sphere inside of which ten powerful laser beams converge. (b) The target itself is a tiny capsule (1 mm in diameter) of deuterium mixed with tritium. A laser pulse one billionth of a second in duration heats the target hotter than the sun's core, raising its pressure to more than 100 million atm, to initiate nuclear fusion.

(a, © Phototake; b, Courtesy of the University of California, Lawrence Livermore National Laboratory, and the U.S. Department of Energy)

with a predicted energy release of 17.6 MeV. The neutrons produced in this reaction can be used to make the needed tritium by means of the reaction

$$^{6}_{3}\text{Li} + ^{1}_{0}n \longrightarrow ^{3}_{1}\text{H} + ^{4}_{2}\text{He}$$

in a lithium "blanket" that surrounds the region of the reaction. Temperatures on the order of 10^8 K are required to initiate these reactions, by which point atoms are stripped of all their electrons and the system is a plasma (ionized gas) of nuclei, electrons, and neutrons. There are two major problems: heating the plasma to this high temperature and confining it. In a laser fusion reactor, pellets of deuterium–tritium fuel are raised to the thermonuclear ignition temperature by bursts of light fired from lasers (Fig. 19.13). Contact between the plasma and the wall of the confining vessel would immediately result in prohibitive energy losses and extinguish the fusion reaction. A plasma can be contained in an intense toroidal (doughnut-shaped) magnetic field. Research reactors using this confinement method have progressed and are reaching the point where they produce more energy than they consume. Formidable problems still must be solved, including the development of materials for containment vessels that can withstand the corrosive effects of the intense x-ray and neutron radiation that is present.

The rewards of a workable nuclear fusion process would be great. Fusion produces neither the long-lived radioactive nuclides that accompany nuclear fission (although tritium requires care in handling) nor the environmental pollutants released by the burning of fossil fuels. Although deuterium is present in only 1/6000 of the abundance of ordinary hydrogen, its separation from the latter by the electrolysis of water is readily accomplished, and the oceans contain a virtually unlimited quantity of deuterium.

CHAPTER SUMMARY

The identities of the elements are not preserved in nuclear reactions—elements decay into lighter daughter elements in fission reactions and heavier elements are synthesized from lighter elements in fusion reactions. Mass changes in nuclear reactions are relatively small, but the accompanying energy changes are enormous; they are related by Einstein's famous formula $E = mc^2$. The isotopes of the lighter elements ($Z < 40$ or so) are stable when the ratio of the number of neutrons to the number of protons (N/Z) is approximately equal to 1. Isotopes with $N/Z < 1$ will decay via positron emission or electron capture to increase the number of protons in the nucleus, whereas those with $N/Z > 1$ will decay via beta emission to decrease the number of protons in the nucleus. A fourth decay channel, alpha particle emission, becomes important for heavier nuclei. Radioactive decay follows first order kinetics and the half-life $t_{1/2}$ is a convenient measure of the timescale of the reaction. Half-lives range from 10^{-16} s to 10^{10} years, which is an incredibly wide range of timescales. The half-life of ^{238}U has been used to calibrate geological timescales and ^{14}C dating is a well-established method for dating human artifacts in anthropology. X-rays, gamma rays, electrons, positrons, and alpha particles are all used in medical diagnostics and therapy with increasing efficacy and fewer side effects. Nuclear fusion, which led to the formation of the heavier elements from hydrogen in the process called nucleosynthesis, continues to hold promise as a source of clean power for the future.

CUMULATIVE EXERCISE

Radon

Radioactive ^{222}Rn and ^{220}Rn form constantly from the decay of uranium and thorium in rocks and soil and, being gaseous, seep out of the ground. The radon isotopes decay fairly quickly, but their products, which are also radioactive, are then in the air and attach themselves to dust particles. Thus, airborne radioactivity can accumulate to worrisome levels in poorly ventilated basements in ground that is rich in uranium and thorium.

(a) Describe the composition of an atom of ^{222}Rn and compare it with that of an atom of ^{220}Rn.

(b) Although ^{222}Rn is a decay product of ^{238}U, ^{220}Rn comes from ^{232}Th. How many alpha particles are emitted in the formation of these radon isotopes from their uranium or thorium starting points? (*Hint:* Alpha decay changes the mass number *A*, but other decay processes do not.)

(c) Can alpha decay alone explain the formation of these radon isotopes from ^{238}U and ^{232}Th? If not, state what other types of decay must occur.

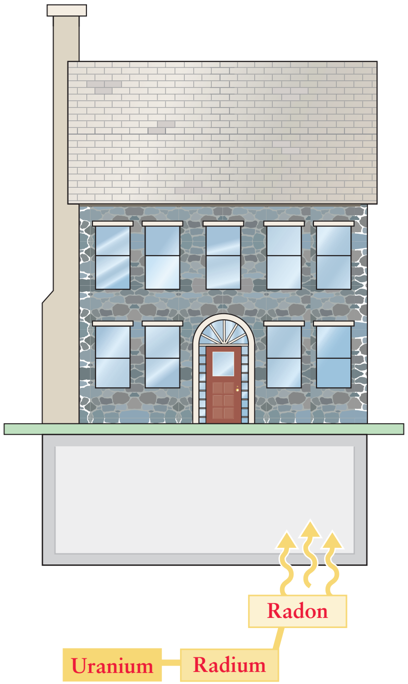
(d) Can $^{222}_{86}$Rn and $^{220}_{86}$Rn decay by alpha particle emission? Write balanced nuclear equations for these two decay processes, and calculate the changes in mass that would result. The masses of ^{222}Rn and ^{220}Rn atoms are 222.01757 and 220.01140 u, respectively; those of ^{218}Po and ^{216}Po are 218.0089 and 216.00192 u, respectively.

(e) Calculate the energy change in the alpha decay of one ^{220}Rn nucleus, in million electron volts and in joules.

(f) The half-life of ^{222}Rn is 3.82 days. Calculate the initial activity of 2.00×10^{-8} g of ^{222}Rn, in disintegrations per second.

(g) What will be the activity of the ^{222}Rn from part (f) after 14 days?

(h) The half-life of ^{220}Rn is 54 s. Are the health risks of exposure to a given amount of radon for a given short length of time greater or smaller for ^{220}Rn than for ^{222}Rn?



Radon most commonly enters houses through the foundation or basement walls.

Answers

(a) An atom of ^{222}Rn has 86 electrons outside the nucleus. Inside the nucleus are 86 protons and $222 - 86 = 136$ neutrons. An atom of ^{220}Rn has the same number of electrons and protons, but only 134 neutrons in its nucleus.

(b) Four alpha particles are produced to make ^{222}Rn from ^{238}U; three are produced to make ^{220}Rn from ^{232}Th.

(c) If $^{238}_{92}\text{U}$ were to lose four alpha particles, $^{222}_{84}\text{Po}$ would result instead of $^{222}_{84}\text{Rn}$. Two $^{0}_{-1}e^{-}$ beta particles must be ejected from the nucleus along the way to raise the atomic number to $Z = 86$. The same is true of the production of ^{220}Rn from ^{232}Th.

(d) $^{222}_{86}\text{Rn} \longrightarrow {}^{218}_{84}\text{Po} + {}^{4}_{2}\text{He}$; $\Delta m = -0.00617 \text{ u} < 0$; allowed

$^{220}_{86}\text{Rn} \longrightarrow {}^{216}_{84}\text{Po} + {}^{4}_{2}\text{He}$; $\Delta m = -0.0069 \text{ u} < 0$; allowed

(e) $\Delta E = -6.4 \text{ MeV} = -1.03 \times 10^{-12} \text{ J}$

(f) $A = 1.14 \times 10^{8} \text{ s}^{-1}$

(g) $A = 9.0 \times 10^{6} \text{ s}^{-1}$

(h) Greater

CHAPTER REVIEW

- One atomic mass unit (u) is $1.6605 \text{ x } 10^{-27}$ kg.
- The energy change ΔE that results from a mass change in a nuclear reaction (Δm) is given by the Einstein mass-energy relationship $\Delta E = c^2 \Delta m$.
- $\Delta E = 931.5$ MeV for $\Delta \text{u} = 1$ so the energy equivalent of 1 u is 931.5 MeV.
- Nuclear reactions are spontaneous when $\Delta E < 0$ because ΔE is so large compared with pressure-volume work or any entropy changes associated with nuclear reactions, making $\Delta G = \Delta E$.
- Electron–positron and proton–antiproton are particle–antiparticle pairs in which the members of each pair have the same masses but opposite charges. The neutrino and antineutrino are neutral particles that form another important particle–antiparticle pair.
- Nuclear decay processes

  The equations for nuclear reactions are balanced using the same methods developed for chemical reactions. Charge, mass, and atomic number are conserved. The electron is assigned an effective atomic number $Z = -1$ for this purpose.

  Beta decay: unstable nuclides with fewer protons than stable nuclides of the same mass number convert neutrons into protons by emitting an electron (beta particle).

  Positron emission: unstable nuclides with more protons than stable nuclides of the same mass number convert protons into neutrons by emitting a positron.

  Electron capture: electron capture is more important than positron emission for converting protons into neutrons when the mass change is less than twice the mass of the positron.

  Alpha decay: very heavy elements can decay by emitting a He nucleus (alpha particle), decreasing the atomic number by 2 and the mass number by 4.
- Radiation detectors

  Photographic film

  Scintillators: particles that emit light when excited by radiation

  Geiger counters: gas tubes designed to produce large current pulses from avalanches of ionized electrons

  Array detectors: scintillators coupled to very large arrays of semiconductor detectors that have largely replaced film in medical diagnostics

- Kinetics of radioactive decay: first order decay with half-life $t_{1/2} = \ln 2/k = 0.693/k$.
- Radioactive dating: living organisms have $^{14}C/^{12}C$ ratios characteristic of the atmosphere of the time. When the organism dies, ^{14}C decays with $t_{1/2} = 5730$ years, enabling dating by counting half-lives.
- Radiation dosimetry in biology and medicine

  rad (radiation adsorbed dose): 10^{-2} J per kg of tissue (S.I. unit gray (Gy) = 100 rad = 1 J per kg)

  rem (roentgen equivalent in man): accounts for relative biological damage (S.I. unit sievert (Sv) = 100 rem by analogy to gray)

  1 rad (beta) $\longrightarrow$ 1 rem

  1 rad (alpha) $\longrightarrow$ 10 rem
- Nuclear chain reactions

  ^{235}U decay produces more than one neutron per disintegration, which can lead to a chain reaction. Rates of fission reactions are controlled using moderators to reduce the energy of the neutrons and enhance the rate and control rods to limit the neutron flux and reduce the rate.

  Fusion of hydrogen isotopes in normal stars produces He, which reacts further to produce all of the heavier elements in a series of fusion reactions called nucleosynthesis.

CONCEPTS & SKILLS

After studying this chapter and working the problems that follow, you should be able to:

1. Calculate the binding energy of a nucleus (Section 19.1, Problems 3–6).
2. Write balanced nuclear equations for beta decay, positron emission, electron capture, and alpha decay processes and calculate the maximum kinetic energies of particles emitted (Section 19.2, Problems 7–18).
3. Describe several methods that are used to detect the products of radioactive decay (Section 19.2).
4. Solve problems involving the half-life or decay constant of a radioactive sample and its activity (Section 19.3, Problems 19–24).
5. Apply the kinetics of nuclear decay to the dating of rocks or artifacts (Section 19.3, Problems 25–30).
6. Discuss the interactions of radiation with various kinds of matter and the measurement of radiation dosage (Section 19.4, Problems 33–36).
7. Describe the processes of nuclear fission and fusion, and calculate the amounts of energy released when they occur (Sections 19.5 and 19.6, Problems 37–47).
8. Explain the benefits and risks associated with the use of nuclear reactions for power generation (Sections 19.5 and 19.6).

KEY EQUATIONS

$$\Delta E = c^2\,\Delta m \qquad \textbf{(Section 19.1)}$$

$$A = -\frac{dN}{dt} = kN \qquad \textbf{(Section 19.3)}$$

$$A = A_i\,e^{-kt} \qquad \textbf{(Section 19.3)}$$

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G. Problems that are more challenging are indicated with asterisks.

Mass–Energy Relationships in Nuclei

1. Complete and balance the following equations for nuclear reactions that are thought to take place in stars:
(a) $2\ {}^{12}_{6}\text{C} \longrightarrow ? + {}^{1}_{0}n$
(b) $? + {}^{1}_{1}\text{H} \longrightarrow {}^{12}_{6}\text{C} + {}^{4}_{2}\text{He}$
(c) $2\ {}^{3}_{2}\text{He} \longrightarrow ? + 2\ {}^{1}_{1}\text{H}$

2. Complete and balance the following equations for nuclear reactions that are used in particle accelerators to make elements beyond uranium:
(a) ${}^{4}_{2}\text{He} + {}^{253}_{99}\text{Es} \longrightarrow ? + 2{}^{1}_{0}n$
(b) ${}^{249}_{98}\text{Cf} + ? \longrightarrow {}^{257}_{103}\text{Lr} + 2\ {}^{1}_{0}n$
(c) ${}^{238}_{92}\text{U} + {}^{12}_{6}\text{C} \longrightarrow {}^{244}_{98}\text{Cf} + ?$

3. Calculate the total binding energy, in both kJ per mole and MeV per atom, and the binding energy per nucleon of the following nuclides, using the data from Table 19.1.
(a) ${}^{40}_{20}\text{Ca}$ (b) ${}^{87}_{37}\text{Rb}$ (c) ${}^{238}_{92}\text{U}$

4. Calculate the total binding energy, in both kilojoules per mole and MeV per atom, and the binding energy per nucleon of the following nuclides, using the data from Table 19.1.
(a) ${}^{10}_{4}\text{Be}$ (b) ${}^{35}_{17}\text{Cl}$ (c) ${}^{49}_{22}\text{Ti}$

5. Use the data from Table 19.1 to predict which is more stable: four protons, four neutrons, and four electrons organized as two ${}^{4}\text{He}$ atoms or as one ${}^{8}\text{Be}$ atom. What is the mass difference?

6. Use the data from Table 19.1 to predict which is more stable: 16 protons, 16 neutrons, and 16 electrons organized as two ${}^{16}\text{O}$ atoms or as one ${}^{32}\text{S}$ atom. What is the mass difference?

Nuclear Decay Processes

7. The nuclide ${}^{8}_{5}\text{B}$ decays by positron emission to ${}^{8}_{4}\text{Be}$. What is the energy released (in MeV)?

8. The nuclide ${}^{10}_{4}\text{Be}$ undergoes spontaneous radioactive decay to ${}^{10}_{5}\text{B}$ with emission of a beta particle. Calculate the maximum kinetic energy of the emitted beta particle.

9. Write balanced equations that represent the following nuclear reactions.
(a) Beta emission by ${}^{39}_{17}\text{Cl}$
(b) Positron emission by ${}^{22}_{11}\text{Na}$
(c) Alpha emission by ${}^{224}_{88}\text{Ra}$
(d) Electron capture by ${}^{82}_{38}\text{Sr}$

10. Write balanced equations that represent the following nuclear reactions.
(a) Alpha emission by ${}^{155}_{70}\text{Yb}$
(b) Positron emission by ${}^{26}_{14}\text{Si}$
(c) Electron capture by ${}^{65}_{30}\text{Zn}$
(d) Beta emission by ${}^{100}_{41}\text{Nb}$

11. The stable isotopes of neon are ${}^{20}\text{Ne}$, ${}^{21}\text{Ne}$, and ${}^{22}\text{Ne}$. Predict the nuclides formed when ${}^{19}\text{Ne}$ and ${}^{23}\text{Ne}$ decay.

12. The two stable isotopes of carbon are ${}^{12}\text{C}$ and ${}^{13}\text{C}$. Predict the nuclides formed when ${}^{11}\text{C}$ and ${}^{14}\text{C}$ decay. Is alpha emission by ${}^{14}\text{C}$ possible?

13. The free neutron is an unstable particle that decays into a proton. What other particle is formed in neutron decay, and what is the maximum kinetic energy (in MeV) that it can possess?

14. The radionuclide ${}^{210}_{84}\text{Po}$ decays by alpha emission to a daughter nuclide. The atomic mass of ${}^{210}_{84}\text{Po}$ is 209.9829 u, and that of its daughter is 205.9745 u.
(a) Identify the daughter, and write the nuclear equation for the radioactive decay process.
(b) Calculate the total energy released per disintegration (in MeV).
(c) Calculate the kinetic energy of the emitted alpha particle.

15. The natural abundance of ${}^{30}\text{Si}$ is 3.1%. Upon irradiation with neutrons, this isotope is converted to ${}^{31}\text{Si}$, which decays to the stable isotope ${}^{31}\text{P}$. This provides a way of introducing trace amounts of phosphorus into silicon in a much more uniform fashion than is possible by ordinary mixing of silicon and phosphorus and gives semiconductor devices the capability of handling much higher levels of power. Write balanced nuclear equations for the two steps in the preparation of ${}^{31}\text{P}$ from ${}^{30}\text{Si}$.

16. The most convenient way to prepare the element polonium is to expose bismuth (which is 100% ${}^{209}\text{Bi}$) to neutrons. Write balanced nuclear equations for the two steps in the preparation of polonium.

17. One convenient source of neutrons is the reaction of an alpha particle from an emitter such as polonium (${}^{210}\text{Po}$) with an atom of beryllium (${}^{9}\text{Be}$). Write nuclear equations for the reactions that occur.

18. Three atoms of element 111 were produced in 1994 by bombarding ${}^{209}\text{Bi}$ with ${}^{64}\text{Ni}$.
(a) Write a balanced equation for this nuclear reaction. What other species is produced?
(b) Write a balanced equation for the alpha decay process of this nuclide of element 111.

Kinetics of Radioactive Decay

19. How many radioactive disintegrations occur per minute in a 0.0010-g sample of ${}^{209}\text{Po}$ that has been freshly separated from its decay products? The half-life of ${}^{209}\text{Po}$ is 103 years.

20. How many alpha particles are emitted per minute by a 0.0010-g sample of ${}^{238}\text{U}$ that has been freshly separated from its decay products? Assume that each decay emits one alpha particle. The half-life of ${}^{238}\text{U}$ is 4.47×10^{9} years.

21. The nuclide ${}^{19}\text{O}$, prepared by neutron irradiation of ${}^{19}\text{F}$, has a half-life of 29 s.
(a) How many ${}^{19}\text{O}$ atoms are in a freshly prepared sample if its decay rate is $2.5 \times 10^{4}\ \text{s}^{-1}$?
(b) After 2.00 min, how many ${}^{19}\text{O}$ atoms remain?

22. The nuclide ${}^{35}\text{S}$ decays by beta emission with a half-life of 87.1 days.
(a) How many grams of ${}^{35}\text{S}$ are in a sample that has a decay rate from that nuclide of $3.70 \times 10^{2}\ \text{s}^{-1}$?
(b) After 365 days, how many grams of ${}^{35}\text{S}$ remain?

23. Astatine is the rarest naturally occurring element, with ${}^{219}\text{At}$ appearing as the product of a very minor side branch in the decay of ^{235}U (itself not a very abundant isotope). It is estimated that the mass of all the naturally occurring ^{219}At in the upper kilometer of the earth's surface has a steady-state value of only 44 mg. Calculate the total activity (in disintegrations per second) caused by all the naturally occurring astatine in this part of the earth. The half-life of ^{219}At is 54 s, and its atomic mass is 219.01 u.

24. Technetium has not been found in nature. It can be obtained readily as a product of uranium fission in nuclear power plants, however, and is now produced in quantities of many kilograms per year. One medical use relies on the tendency of ^{99m}Tc (an excited nuclear state of ^{99}Tc) to concentrate in abnormal heart tissue. Calculate the total activity (in disintegrations per second) caused by the decay of 1.0 μg of ^{99m}Tc, which has a half-life of 6.0 hours.

25. The specific activity of ^{14}C in the biosphere is 0.255 Bq g^{-1}. What is the age of a piece of papyrus from an Egyptian tomb if its beta counting rate is 0.153 Bq g^{-1}? The half-life of ^{14}C is 5730 years.

26. The specific activity of an article found in the Lascaux Caves in France is 0.0375 Bq g^{-1}. Calculate the age of the article.

27. Over geological time, an atom of ^{238}U decays to a stable ^{206}Pb atom in a series of eight alpha emissions, each of which leads to the formation of one helium atom. A geochemist analyzes a rock and finds that it contains 9.0×10^{-5} cm^3 of helium (at 0°C and atmospheric pressure) per gram and 2.0×10^{-7} g of ^{238}U per gram. Estimate the age of the mineral, given that $t_{1/2}$ of ^{238}U is 4.47×10^9 years.

28. The isotope ^{232}Th decays to ^{208}Pb by the emission of six alpha particles, with a half-life of 1.39×10^{10} years. Analysis of 1.00 kg of ocean sediment shows it to contain 7.4 mg of ^{232}Th and 4.9×10^{-3} cm^3 of gaseous helium at 0°C and atmospheric pressure. Estimate the age of the sediment, assuming no loss or gain of thorium or helium from the sediment since its formation and assuming that the helium arose entirely from the decay of thorium.

29. The half-lives of ^{235}U and ^{238}U are 7.04×10^8 years and 4.47×10^9 years, respectively, and the present abundance ratio is $^{238}\text{U}/^{235}\text{U} = 137.7$. It is thought that their abundance ratio was 1 at some time *before* our earth and solar system were formed about 4.5×10^9 years ago. Estimate how long ago the supernova occurred that supposedly produced all the uranium isotopes in equal abundance, including the two longest lived isotopes, ^{238}U and ^{235}U.

30. Using the result of problem 29 and the accepted age of the earth, 4.5×10^9 yr, calculate the $^{238}\text{U}/^{235}\text{U}$ ratio at the time the earth was formed.

Radiation in Biology and Medicine

31. Write balanced equations for the decays of ^{11}C and ^{15}O, both of which are used in positron emission tomography to scan the uptake of glucose in the body.

32. Write balanced equations for the decays of ^{13}N and ^{18}F, two other radioisotopes that are used in positron emission tomography. What is the ultimate fate of the positrons?

33. The positrons emitted by ^{11}C have a maximum kinetic energy of 0.99 MeV, and those emitted by ^{15}O have a maximum kinetic energy of 1.72 MeV. Calculate the ratio of the number of millisieverts of radiation exposure caused by ingesting a given fixed chemical amount (equal numbers of atoms) of each of these radioisotopes.

34. Compare the relative health risks of contact with a given amount of ^{226}Ra, which has a half-life of 1622 years and emits 4.78-MeV alpha particles, with contact with the same chemical amount of ^{14}C, which has a half-life of 5730 years and emits beta particles with energies of up to 0.155 MeV.

35. The nuclide ^{131}I undergoes beta decay with a half-life of 8.041 days. Large quantities of this nuclide were released into the environment in the Chernobyl accident. A victim of radiation poisoning has absorbed 5.0×10^{-6} g (5.0 μg) of ^{131}I.

(a) Compute the activity, in becquerels, of the ^{131}I in this person, taking the atomic mass of the nuclide to equal 131 g mol^{-1}.

(b) Compute the radiation absorbed dose, in milligrays, caused by this nuclide during the first *second* after its ingestion. Assume that beta particles emitted by ^{131}I have an average kinetic energy of 0.40 MeV, that all of this energy is deposited within the victim's body, and that the victim weighs 60 kg.

(c) Is this dose likely to be lethal? Remember that the activity of the ^{131}I diminishes as it decays.

36. The nuclide ^{239}Pu undergoes alpha decay with a half-life of 2.411×10^4 years. An atomic energy worker breathes in 5.0×10^{-6} g (5.0 μg) of ^{239}Pu, which lodges permanently in a lung.

(a) Compute the activity, in becquerels, of the ^{239}Pu ingested, taking the atomic mass of the nuclide to be 239 g mol^{-1}.

(b) Determine the radiation absorbed dose, in milligrays, during the first *year* after its ingestion. Assume that alpha particles emitted by ^{239}Pu have an average kinetic energy of 5.24 MeV, that all of this energy is deposited within the worker's body, and that the worker weighs 60 kg.

(c) Is this dose likely to be lethal?

Nuclear Fission

37. Strontium-90 is one of the most hazardous products of atomic weapons testing because of its long half-life ($t_{1/2}$ = 28.1 years) and its tendency to accumulate in bone.

(a) Write nuclear equations for the decay of ^{90}Sr via the successive emission of two beta particles.

(b) The atomic mass of ^{90}Sr is 89.9073 u and that of ^{90}Zr is 89.9043 u. Calculate the energy released per ^{90}Sr atom, in MeV, in decaying to ^{90}Zr.

(c) What will be the initial activity of 1.00 g of ^{90}Sr released into the environment, in disintegrations per second?

(d) What activity will the material from part (c) show after 100 years?

38. Plutonium-239 is the fissionable isotope produced in breeder reactors; it is also produced in ordinary nuclear plants and in weapons tests. It is an extremely poisonous substance with a half-life of 24,100 years.

(a) Write an equation for the decay of ^{239}Pu via alpha emission.

(b) The atomic mass of ^{239}Pu is 239.05216 u and that of ^{235}U is 235.04393 u. Calculate the energy released per ^{239}Pu atom, in MeV, in decaying via alpha emission.

(c) What will be the initial activity, in disintegrations per second, of 1.00 g of ^{239}Pu buried in a disposal site for radioactive wastes?

(d) What activity will the material from part (c) show after 100,000 years?

39. The three naturally occurring isotopes of uranium are ^{234}U (half-life 2.5×10^5 years), ^{235}U (half-life 7.0×10^8 years), and ^{238}U (half-life 4.5×10^9 years). As time passes, will the average atomic mass of the uranium in a sample taken from nature increase, decrease, or remain constant?

40. Natural lithium consists of 7.42% ^{6}Li and 92.58% ^{7}Li. Much of the tritium ($^3_1$H) used in experiments with fusion reactions is made by the capture of neutrons by ^{6}Li atoms.

(a) Write a balanced nuclear equation for the process. What is the other particle produced?

(b) After ^{6}Li is removed from natural lithium, the remainder is sold for other uses. Is the molar mass of the leftover lithium greater or smaller than that of natural lithium?

41. Calculate the amount of energy released, in kilojoules per *gram* of uranium, in the fission reaction

$$^{235}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{94}_{36}\text{Kr} + {}^{130}_{56}\text{Ba} + 3\,{}^{1}_{0}n$$

Use the atomic masses in Table 19.1. The atomic mass of ^{94}Kr is 93.919 u and that of ^{139}Ba is 138.909 u.

Nuclear Fusion and Nucleosynthesis

42. Calculate the amount of energy released, in kilojoules per *gram* of deuterium (^{2}H), for the fusion reaction

$$^{2}_{1}\text{H} + {}^{2}_{1}\text{H} \longrightarrow \; + {}^{4}_{2}\text{He}$$

Use the atomic masses in Table 19.1. Compare your answer with that from the preceding problem.

ADDITIONAL PROBLEMS

43. When an electron and a positron meet, they are replaced by two gamma rays, called the "annihilation radiation." Calculate the energies of these radiations, assuming that the kinetic energies of the incoming particles are 0.

44. The nuclide $^{231}_{92}$U converts spontaneously to$^{231}_{91}$Pa.

(a) Write two balanced nuclear equations for this conversion, one if it proceeds by electron capture and the other if it proceeds by positron emission.

(b) Using the nuclidic masses in Table 19.1, calculate the change in mass for each process. Explain why electron capture can occur spontaneously in this case but positron emission cannot.

45. The radioactive nuclide $^{64}_{29}$Cu decays by beta emission to $^{64}_{30}$Zn or by positron emission to $^{64}_{28}$Ni. The maximum kinetic energy of the beta particles is 0.58 MeV, and that of the positrons is 0.65 MeV. The mass of the neutral $^{64}_{29}$Cu atom is 63.92976 u.

(a) Calculate the mass, in atomic mass units, of the neutral $^{64}_{30}$Zn atom.

(b) Calculate the mass, in atomic mass units, of the neutral $^{64}_{28}$Ni atom.

46. A puzzling observation that led to the discovery of isotopes was the fact that lead obtained from uranium-containing ores had an atomic mass lower by two full atomic mass units than lead obtained from thorium-containing ores. Explain this result, using the fact that decay of radioactive uranium and thorium to stable lead occurs via alpha and beta emission.

47. By 1913, the elements radium, actinium, thorium, and uranium had all been discovered, but element 91, between thorium and uranium in the periodic table, was not yet known. The approach used by Meitner and Hahn was to look for the parent that decays to form actinium. Alpha and beta emission are the most important decay pathways among the heavy radioactive elements. What elements would decay to actinium by each of these two pathways? If radium salts show no sign of actinium, what does this suggest about the parent of actinium? What is the origin of the name of element 91, discovered by Meitner and Hahn in 1918?

48. Working in Rutherford's laboratory in 1932, Cockcroft and Walton bombarded a lithium target with 700-keV protons and found that the following reaction occurred:

$$^{7}_{3}\text{Li} + {}^{1}_{1}\text{H} \longrightarrow \; + 2\,{}^{4}_{2}\text{He}$$

Each of the alpha particles was found to have a kinetic energy of 8.5 MeV. This research provided the first experimental test of Einstein's $\Delta E = c^2 \Delta m$ relationship. Discuss. Using the atomic masses from Table 19.1, calculate the value of c needed to account for this result.

49. **(a)** Calculate the binding energy per nucleon in $^{30}_{15}$P.

(b) The radioactive decay of the $^{30}_{15}$P occurs through positron emission. Calculate the maximum kinetic energy carried off by the positron.

(c) The half-life for this decay is 150 s. Calculate the rate constant k and the fraction remaining after 450 s.

50. Selenium-82 undergoes *double* beta decay:

$$^{82}_{34}\text{Se} \longrightarrow {}^{82}_{36}\text{Kr} + 2\,{}^{0}_{-1}e^{-} + 2\tilde{\nu}$$

This low-probability process occurs with a half-life of 3.5×10^{27} s, one of the longest half-lives ever measured. Estimate the activity in an 82.0-g (1.00 mol) sample of this isotope. How many ^{82}Se nuclei decay in a day?

51. Gallium citrate, which contains the radioactive nuclide ^{67}Ga, is used in medicine as a tumor-seeking agent. Gallium-67 decays with a half-life of 77.9 hours. How much time is required for it to decay to 5.0% of its initial activity?

52. The nuclide ^{241}Am is used in smoke detectors. As it decays (with a half-life of 458 years), the emitted alpha particles ionize the air. When combustion products enter the detector, the number of ions changes and with it the conductivity of the air, setting off an alarm. If the activity of ^{241}Am in the detector is 3×10^4 Bq, calculate the mass of ^{241}Am present.

53. The half-life of ^{14}C is $t_{1/2} = 5730$ years, and 1.00 g of modern wood charcoal has an activity of 0.255 Bq.

(a) Calculate the number of ^{14}C atoms per gram of carbon in modern wood charcoal.

(b) Calculate the fraction of carbon atoms in the biosphere that are ^{14}C.

54. Carbon-14 is produced in the upper atmosphere by the reaction

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$$

where the neutrons come from nuclear processes induced by cosmic rays. It is estimated that the steady-state ^{14}C activity in the biosphere is 1.1×10^{19} Bq.

(a) Estimate the total mass of carbon in the biosphere, using the data in problem 53.

(b) The earth's crust has an average carbon content of 250 parts per million by mass, and the total crustal mass is 2.9×10^{25} g. Estimate the fraction of the carbon in the earth's crust that is part of the biosphere. Speculate on the whereabouts of the rest of the carbon in the earth's crust.

55. Analysis of a rock sample shows that it contains 0.42 mg of ^{40}Ar for every 1.00 mg of ^{40}K. Assuming that all the argon resulted from decay of the potassium and that neither element has left or entered the rock since its formation, estimate the age of the rock. (*Hint:* Use data from Table 19.2.) Note that not all the ^{40}K decays to ^{40}Ar.

* **56.** Cobalt-60 and iodine-131 are used in treatments for some types of cancer. Cobalt-60 decays with a half-life of 5.27 years, emitting beta particles with a maximum energy of 0.32 MeV. Iodine-131 decays with a half-life of 8.04 days, emitting beta particles with a maximum energy of 0.60 MeV.

(a) Suppose a fixed small number of moles of each of these isotopes were to be ingested and remain in the body indefinitely. What is the *ratio* of the number of millisieverts of total lifetime radiation exposure that would be caused by the two radioisotopes?

(b) Now suppose that the contact with each of these isotopes is for a fixed short period, such as 1 hour. What is the ratio of millisieverts of radiation exposure for the two in this case?

57. Boron is used in control rods in nuclear power reactors because it is a good neutron absorber. When the isotope ^{10}B captures a neutron, an alpha particle (helium nucleus) is emitted. What other atom is formed? Write a balanced equation.

* **58.** The average energy released in the fission of a ^{235}U nucleus is about 200 MeV. Suppose the conversion of this energy to electrical energy is 40% efficient. What mass of ^{235}U is converted to its fission products in a year's operation of a 1000-megawatt nuclear power station? Recall that 1 W is 1 J s^{-1}.

59. The energy released by a bomb is sometimes expressed in tons of TNT (trinitrotoluene). When one ton of TNT explodes, 4×10^9 J of energy is released. The fission of 1 mol of uranium releases approximately 2×10^{13} J of energy. Calculate the energy released by the fission of 1.2 kg of uranium in a small atomic bomb. Express your answer in tons of TNT.

60. The solar system abundances of the elements Li, Be, and B are four to seven orders of magnitude lower than those of the elements that immediately follow them: C, N, and O. Explain.

* **61.** The sun's distance from earth is approximately 1.50×10^8 km, and the earth's radius is 6371 km. The earth receives radiant energy from hydrogen burning in the sun at a rate of $0.135 \text{ J s}^{-1} \text{ cm}^{-2}$. Using the data of Table 19.1, calculate the mass of hydrogen converted per second in the sun.

CUMULATIVE PROBLEMS

62. In 1951 wood from two sequoia trees was dated by the ^{14}C method. In one tree, clean borings located between the growth rings associated with the years A.D. 1057 and 1087 (that is, wood known to have grown 880 ± 15 year prior to the date of measurement) had a ^{14}C activity about 0.892 of that of wood growing in 1951. A sample from a second tree had an activity about 0.838 of that of new wood, and its age was established as 1377 ± 4 year by tree-ring counting.

(a) What ages does carbon dating associate with the wood samples?

(b) What values of $t_{1/2}$ can be deduced if the tree-ring dates given are used as the starting point?

(c) Discuss assumptions underlying the calculations in (a) and (b), and indicate in what direction failures of these assumptions might affect the calculations.

63. A typical electrical generating plant has a capacity of 500 megawatt (MW; $1 \text{ MW} = 10^6 \text{ J s}^{-1}$) and an overall efficiency of about 25%. (a) The combustion of 1 kg of bituminous coal releases about 3.2×10^4 kJ and leaves an ash residue of 100 g. What weight of coal must be used to operate a 500-MW generating plant for 1 year, and what weight of ash must be disposed of? (b) Enriched fuel for nuclear reactors contains about 4% ^{235}U, fission of which gives 1.9×10^{10} kJ per mole ^{235}U. What weight of ^{235}U is needed to operate a 500-MW power plant, assumed to have 25% efficiency, for 1 year, and what weight of fuel must be reprocessed to remove radioactive wastes? (c) The radiation from the sun striking the earth's surface on a sunny day corresponds to a power of 1.5 kW m^{-2}. How large must the collection surface be for a 500-MW solar-generating plant? (Assume that there are 6 hours of bright sun each day and that storage facilities continue to produce power at other times. The efficiency for solar-power generation would be about 25%.)

64. Examine the ratio of atomic mass to atomic number for the elements with *even* atomic number through calcium. This ratio is approximately the ratio of the average mass number to the atomic number.

(a) Which two elements stand out as different in this set of ten?

(b) What would be the "expected" atomic mass of argon, based on the correlation considered here?

(c) Show how the anomaly in the ordering of natural atomic masses of argon and potassium can be accounted for by the formation of "extra" ^{40}Ar via decay of ^{40}K atoms.

65. Hydrazine, $N_2H_4(\ell)$, reacts with oxygen in a rocket engine to form nitrogen and water vapor:

$$N_2H_4(\ell) + O_2(g) \longrightarrow N_2(g) + 2\ H_2O(g)$$

(a) Calculate $\Delta H°$ for this highly exothermic reaction at 25°C, using data from Appendix D.
(b) Calculate $\Delta U°$ of this reaction at 25°C.
(c) Calculate the total change in mass, in grams, during the reaction of 1.00 mol of hydrazine.

66. The long-lived isotope of radium, ^{226}Ra, decays by alpha particle emission to its daughter radon, ^{222}Rn, with a half-life of 1622 years. The energy of the alpha particle is 4.79 MeV. Suppose 1.00 g of ^{226}Ra, freed of all its radioactive progeny, were placed in a calorimeter that contained 10.0 g of water, initially at 25°C. Neglecting the heat capacity of the calorimeter and heat loss to the surroundings, calculate the temperature the water would reach after 1.00 hour. Take the specific heat of water to be 4.18 J K^{-1} g^{-1}.

67. The radioactive nuclide $^{232}_{90}Th$ has a half-life of 1.39×10^{10} years. It decays by a series of consecutive steps, the first two of which involve $^{228}_{88}Ra$ (half-life 6.7 years) and $^{228}_{89}Ac$ (half-life 6.13 hours).

(a) Write balanced equations for the first two steps in the decay of ^{232}Th, indicating all decay products. Calculate the total kinetic energy carried off by the decay products.
(b) After a short initial time, the rate of formation of ^{228}Ra becomes equal to its rate of decay. Express the number of ^{228}Ra nuclei in terms of the number of ^{232}Th nuclei, using the steady-state approximation from Section 18.4.

68. Zirconium is used in the fuel rods of most nuclear power plants. The following half-cell reduction potential applies to aqueous acidic solution:

$$ZrO_2(s) + 4\ H_3O^+(aq) + 4e^- \longrightarrow Zr(s) + 6H_2O\ (\ell) \qquad \mathscr{E}° = -1.43\ \text{V}$$

(a) Predict whether zirconium can reduce water to hydrogen. Write a balanced equation for the overall reaction.
(b) Calculate $\Delta\mathscr{E}°$ and K for the reaction in part (a).
(c) Can your answer to part (b) explain the release of hydrogen in the Three Mile Island accident and the much greater release of hydrogen (which subsequently exploded) at Chernobyl?

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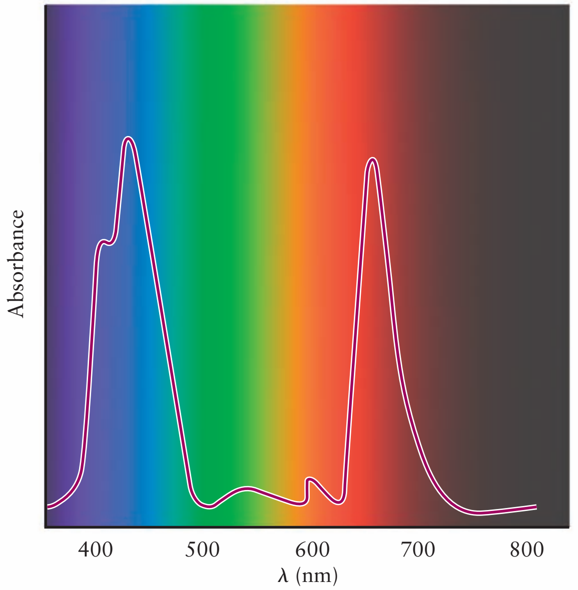
CHAPTER 20

Interaction of Molecules with Light



Optical absorption spectrum of chlorophyll *a* superimposed on the solar spectrum, showing how efficiently this key photosynthetic pigment absorbs a significant fraction of the available light. The color of green leaves is due to chlorophyll's relatively weak abosorption of green light.

Molecules have definite three-dimensional structure, described by their bond lengths and bond angles and determined by the covalent bonds that hold the molecules together. Lewis's electron dot diagrams rationalize the formation of particular compounds, and VSEPR theory rationalizes their structures (see Chapter 3). The quantum theory fully explains the covalent bond, and in its quantitative form predicts the structures and energy levels of the molecules (see Chapter 6). Despite these theoretical advances, there is still a need for experimental determination of molecular structure. Molecular structure is determined by x-ray diffraction in solid-state samples (see Chapter 21), by molecular spectroscopy (the absorption and emission of light by molecules), and by magnetic resonance spectroscopy (the absorption and emission of long-wavelength electromagnetic radiation by molecules in the presence of a magnetic field). In this chapter we survey the spectroscopy techniques that depend on interaction of molecules with light, and we summarize the molecular properties they determine:

1. Bond length, from rotational spectroscopy
2. Bond force constant, from vibrational spectroscopy

3. Pathways of energy flow through molecules, from electronic excitation
4. Identification of bonding groups and their interactions, from magnetic resonance spectroscopy

Light also plays crucial roles in changing molecules by transferring the energy that causes bonds to break or rearrange and by inducing chemical reactions via photochemical pathways very different from ordinary thermochemical pathways. We provide a brief introduction to photochemistry by examining photochemical events that are modifying the properties of the atmosphere of the earth. Light from the sun is the ultimate source for almost all the energy used on the earth. The atmosphere plays a crucial role in transmitting some radiation from the sun to the surface of the earth and absorbing other portions or reradiating them into space. Living species have transformed the composition of the atmosphere over the last 200 years, and industrialization has accelerated the rate of change. These changes raise questions about the sustainability of life on the earth, should present trends continue, and demonstrate the need for enlightened management of energy resources and consumption.

We conclude this chapter with a brief introduction to **photosynthesis,** the natural process through which light energy from the sun is harvested by plants. Energy stored in plants is converted to other forms by combustion, which is one contributor to the changes induced in the atmosphere through industrialization.

20.1 General Aspects of Molecular Spectroscopy

In Chapter 5 we discussed atomic spectroscopy and showed how the frequencies of the light absorbed or emitted by an atom are related to the energy differences between the atom's quantum states. In particular, the spectrum of the hydrogen atom can be interpreted in terms of solutions of the Schrödinger equation for that atom. Because molecules include several nuclei as well as electrons, their internal motions are more complicated than those of atoms, and their energy-level diagrams and spectra consequently exhibit new features not seen in those for atoms. Analysis of these features gives useful information about molecular structure, bond lengths, and bond energies (Table 20.1). Along with diffraction, molecular spectroscopy is a main source of experimental information about chemical bonding and the structure and shape of molecules.

Molecular Energy Levels

The Born–Oppenheimer approximation (see Section 6.1) treats the motion of electrons and nuclei on very different time scales. The electrons, being much less massive, move much more rapidly than the nuclei in a molecule. In the Born–Oppenheimer approximation, we consider the nuclei to be frozen at particular locations and calculate the electronic energy levels and wave functions (molecular orbitals) for the rapidly moving electrons (see Chapter 6). We find that the allowed

TABLE 20.1 Spectroscopic Experiments

Spectral Region	Frequency (s^{-1})	Energy Levels Involved	Information Obtained
Radio waves	10^7–10^9	Nuclear spin states	Electronic structure near the nucleus
Microwave, far infrared	10^9–10^{12}	Rotational	Bond lengths and bond angles
Near infrared	10^{12}–10^{14}	Vibrational	Stiffness of bonds
Visible, ultraviolet	10^{14}–10^{17}	Valence electrons	Electron configuration
X-ray	10^{17}–10^{19}	Core electrons	Core electron energies

energy levels for the electrons depend explicitly on the positions of the frozen nuclei. Then we turn the problem around. In a particular electronic state, we consider the bonding energy of the rapidly moving electrons plus the nuclear–nuclear repulsion to be the potential energy function that governs the motions (vibrations and rotations) of the more sluggish nuclei. Therefore, each quantized energy state for the electrons will have an associated set of quantized vibrational and rotational energy states for the nuclei. Figure 20.1 schematically illustrates the Born–Oppenheimer picture for the energy levels of a typical diatomic molecule. Two electronic states with numerous rotational and vibrational states are shown. The separation between electronic states is much greater than that for rotational and vibrational states. Transitions between electronic states involve absorption or emission of electromagnetic radiation in the visible and ultraviolet regions of the electromagnetic spectrum. Transitions between rotational states involve microwave radiation, and infrared radiation accompanies transitions between vibration states. Rotation of the molecule as a rigid body leads to molecular transitions in the microwave region, and vibrational motions of one nucleus relative to another lead to molecular transitions in the infrared region (see Fig. 4.3).

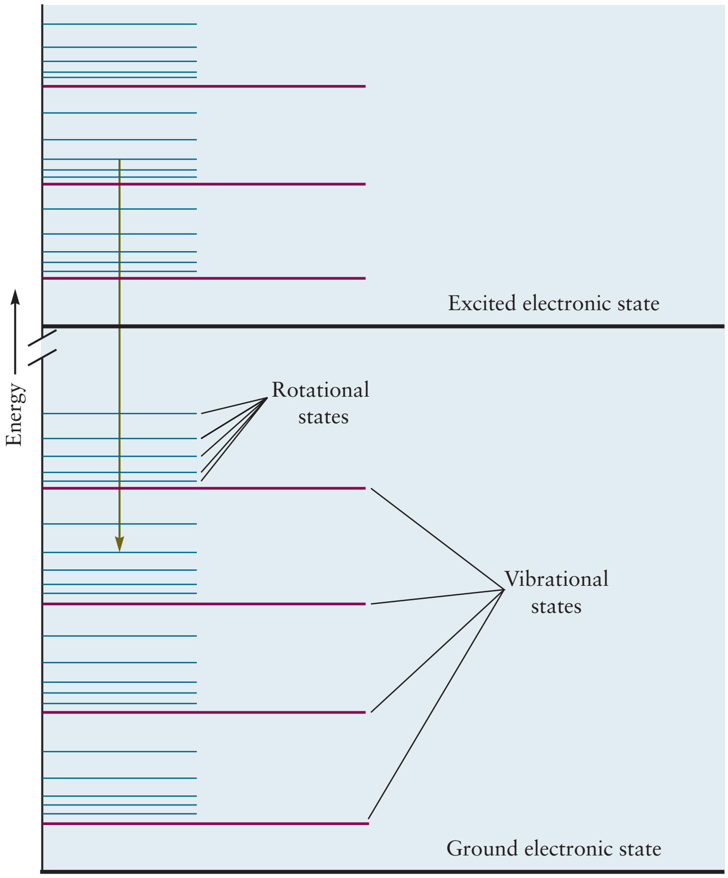
To an excellent level of approximation, the total energy of a molecule can be viewed as the sum of the energies associated with each of these separate motions:

$$E_{\text{tot}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}}$$

When the total energy of a molecule changes during absorption or emission of radiation, the transition usually involves changes in more than one kind of energy. For example, a line in the visible region of the emission spectrum may connect two energy levels that differ in rotational, vibrational, and electronic energy (see the blue arrow in Fig. 20.1).

A polyatomic molecule would have an even more complicated set of energy levels, each characterized by several vibrational quantum numbers and by up to three rotational quantum numbers.

FIGURE 20.1 An energy-level diagram for a diatomic molecule, showing the electronic, vibrational, and rotational levels schematically. The arrow indicates one of the many possible transitions; in this case the rotational, vibrational, and electronic states of the molecule all change.



Experimental Methods in Molecular Spectroscopy

Molecular absorption spectra are recorded by *spectrophotometers* (Fig. 20.2), which differ from the spectrographs illustrated with atomic spectra in Figure 4.9. Light from the source is directed to a prism or grating to select a specific wavelength λ, which then is passed through the sample confined in a cell. The intensity of light transmitted through the sample cell, I_S, is measured. To remove spurious effects due to absorption or scattering of light at the cell walls, the incoming beam is actually split into two parts, one of which is passed through a reference cell of the same size and shape as the sample cell. The spectrophotometer can be calibrated to record a graph of either the **transmittance** $T = I_S/I_R$ or the **absorbance** $A = \ln [I_R/I_S]$ versus λ as wavelength is scanned over the range of interest. The magnitude of the signal is related to properties of the sample as follows. The transmittance T decreases (and the absorbance A increases) as cell length ℓ increases:

$$-\ln \frac{I_S}{I_R} = a\ell = A = -\ln T$$

The parameter a is called the **absorption,** or **extinction, coefficient.** If the sample is a solution, then T decreases and A increases as the concentration c (in mol L^{-1}) of the light-absorbing solute increases, as described by the Beer–Lambert law:

$$-\ln \frac{I_S}{I_R} = c\epsilon\ell = A \qquad [20.1]$$

The parameter ϵ, called the **molar extinction coefficient,** is a property of the light-absorbing solute in the solution; it measures the extent to which that species can absorb light at a particular wavelength.

Peaks in the graph at particular values of λ correspond to transitions between molecular energy levels E_i and E_f that satisfy the relation $\Delta E = E_f - E_i = h\nu = hc/\lambda$. Positions of the peaks correlate with some feature of molecular structure associated with the molecular energy levels E_i and E_f. In principle, these can be identified by solving Schrödinger's equation for the molecule. In practice, they are identified by comparison with extensive tables of spectral data already compiled; the peaks serve as "fingerprints" for identifying structural features. Representative spectra are shown in Figures 20.10, 20.14, and 20.22, which are discussed later.

The area under each peak reflects the concentration of molecules present, as well as the *strength* of the absorption governed by ϵ. This fact is illustrated by the solutions shown in Figure 14.1a and c, in which merely 2% concentration of the blue tetrachloro Co(II) species changes the color of the solution from pink to violet due to its very large molecular extinction coefficient.

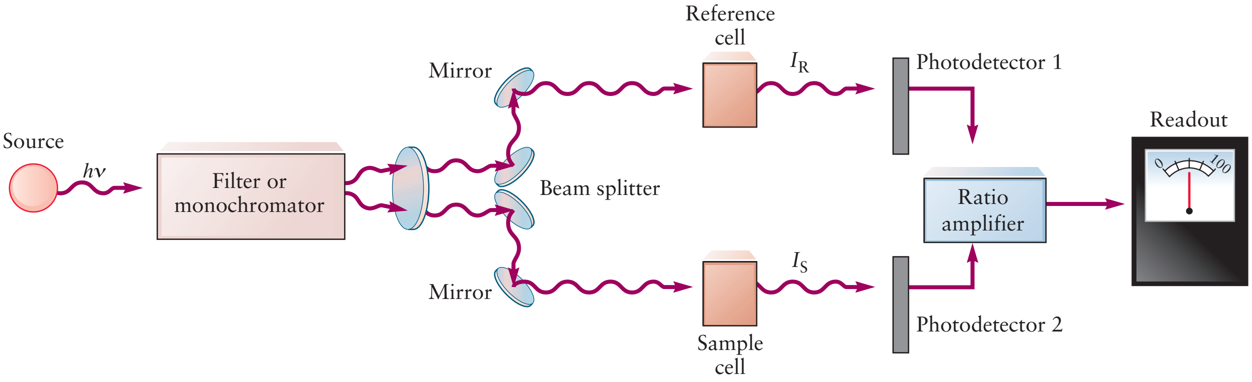


FIGURE 20.2 Schematic of double-beam spectrophotometer. Incoming light passes through a reference cell identical to the sample cell.

The magnitude of ϵ is determined by the strength of the interaction between the absorbing molecule and the light wave and the difference in populations of the initial and final states involved in the transition. Detailed discussion of the interaction of light with molecules requires quantum concepts beyond the scope of this book. The essential physical effect is that the changing dipole moment of the molecule couples with the oscillating electric field of the light wave (see Fig. 4.2) and functions as a "molecular antenna" to absorb energy from the electric field. For energy to be absorbed at a particular wavelength, the number of molecules in the initial state with energy E_i must be greater than the number in the final state with energy E_f.

Thermal Occupation of Molecular Energy Levels

The intensity of an absorption line depends on the strength of the transition and on the population ratio of the initial and final states. The probability that the energy level E_i is occupied is $N(E_i)$, the number of molecules in that level, divided by N_A, the total number of molecules in the system. This is given by the **Boltzmann distribution**

$$P(E_i) = N(E_i)/N_A \propto g(E_i) \exp(-E_i/k_BT) \qquad [20.2]$$

where k_B is the Boltzmann constant, equal to 1.38×10^{-23} J K^{-1} and $g(E_i)$ is the degeneracy of E_i, that is the number of distinct quantum states that correspond to E_i. (See Section 9.6 for an introduction to the Boltzmann distribution and its application to vibrational energy levels of diatomic molecules.) If energies per *mole* are used, k_B is replaced by the gas constant R. This exponential falloff means that at thermal equilibrium very few molecules have energies that are large compared with k_BT.

The population ratio for two energy levels E_i and E_f is

$$P(E_i)/P(E_f) = g(E_i)/g(E_f) \exp[-(E_i - E_f)/k_BT] \qquad [20.3]$$

At room temperature, k_BT has the value 4×10^{-21} J (equivalent to 2.5 kJ mol^{-1}). This is large compared with the typical spacing of rotational levels, so at room temperature many rotational states are occupied in a collection of molecules. This value is also a little smaller than typical vibrational level spacings, so most small molecules at room temperature are in their ground vibrational states, but a measurable fraction occupy excited states. Finally, k_BT is small compared with typical electronic energy spacings, so only the ground electronic state is occupied at room temperature. When molecules are heated, the occupation of more highly excited levels increases.

20.2 Vibrations and Rotations of Molecules: Infrared and Microwave Spectroscopy

Three types of nuclear motion occur in gas-phase molecules: overall translational motion of a molecule through its container, rotational motion in which the molecule turns about one or more axes, and vibrational motion in which the nuclei move relative to each other as bond lengths or angles change. All three motions are subject to the laws of quantum mechanics, but in a gas the translational energy states are so close in energy (they correspond to the particle-in-a-box states of Section 4.6) that quantum effects are not apparent.

In this section we consider the interaction between nuclear motion in molecules and infrared and microwave photons.

Rotations of Molecules

We consider the molecule to be a rigid body, having no distortions in its dimensions while moving. Rotational energies are described in terms of the molecular **moments of inertia** for rotation of the molecule about its center of gravity. (See Appendix B for background on rotational motion.) Figure 20.3 shows the rotational motion for a diatomic molecule, which depends on a single moment of inertia I, defined by

$$I = \mu R_e^2 \qquad [20.4]$$

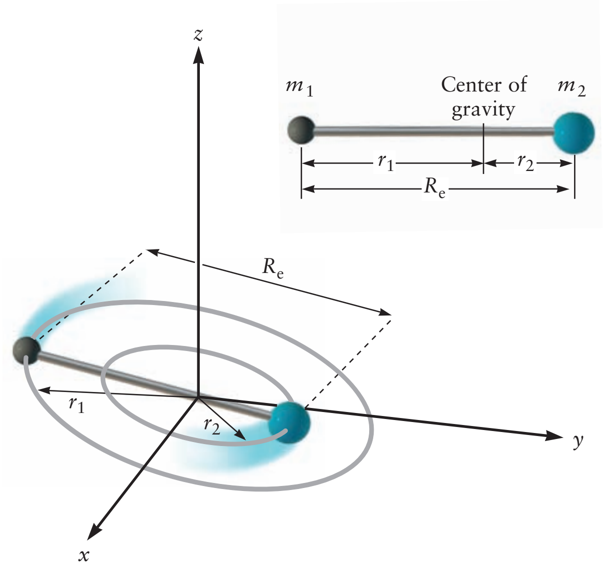
where $\mu = m_1 m_2/(m_1 + m_2)$ is the **reduced mass** of the molecule with m_1 and m_2 being the masses of the two atoms and R_e the bond length. Quantum mechanics demonstrates that rotational motion is quantized and only certain discrete rotational energy levels are permitted. In a linear molecule, the rotational energy can take on only the values

$$E_{\text{rot},J} = \frac{h^2}{8\pi^2 I} J(J+1) = hBJ(J+1) \qquad J = 0, 1, 2, \ldots \qquad [20.5]$$

where J is the rotational quantum number and $B = h/(8\pi^2 I)$. Typical rotational energy differences range from 0.001 kJ mol^{-1} to 1 kJ mol^{-1}. In addition to the energy, the angular momentum of the rotating molecule is also quantized, and the rotational wave function is identical to the angular portion of the hydrogen atom wave functions. For $J = 0$, it resembles an s orbital, for $J = 1$ it resembles p_x, p_y, and p_z orbitals. The degeneracy of the rotational energy levels is $g(E_J) = 2J + 1$.

Radiation in the far (long-wavelength) infrared and microwave regions of the electromagnetic spectrum excites rotational states of molecules. In order to absorb radiation, the molecule must have a permanent dipole moment. Moreover, for a heteronuclear diatomic molecule, absorption of light is possible only between

FIGURE 20.3 A diatomic molecule rotates about its center of gravity. The center of gravity is located by the distances r_1 and r_2, determined from the condition $m_1 r_1 = m_2 r_2$.



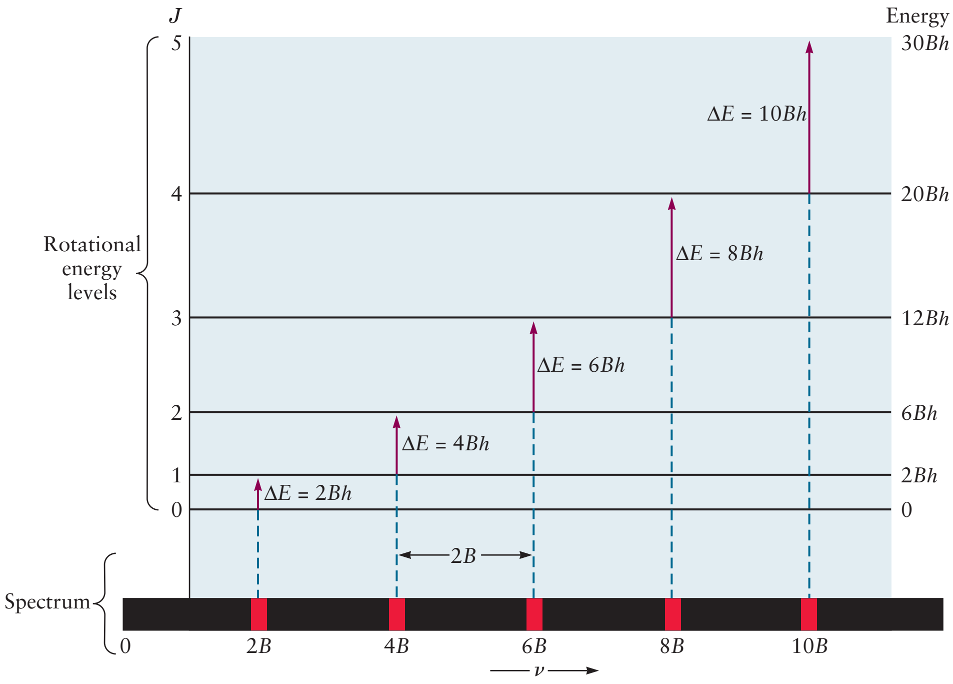


FIGURE 20.4 The energy levels and allowed transitions for rotational motion of a rigid diatomic molecule. The restriction that $\Delta J = +1$ leads to a series of uniformly spaced spectral lines separated in frequency by $2B = 2h/(8\pi^2 I)$. The measured frequency for any one of these lines enables determination of I, as illustrated in Example 20.1.

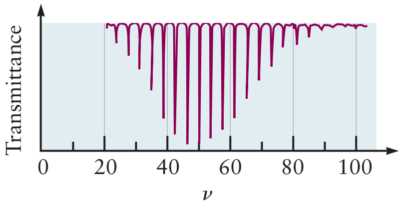


FIGURE 20.5 Schematic representation of an experimental rotational spectrum. Because many rotational states are occupied at room temperature (see Problems 20.9 and 20.10), the measured spectrum includes many of the allowed transitions identified in Figure 20.4.

states that differ by 1 in rotational quantum number ($\Delta J = +1$). The allowed absorption frequencies are

$$\nu = \frac{\Delta E}{h} = \frac{h}{8\pi^2 I}\left[J_f(J_f + 1) - J_i(J_i + 1)\right]$$

$$= \frac{h}{8\pi^2 I}\left[(J_i + 1)(J_i + 2) - J_i(J_i + 1)\right] \qquad [20.6]$$

$$h/8\pi^2 I\,(2J + 2) = 2B(J + 1)$$

because the quantum number of the final rotational state J_f must be 1 greater than that of the initial rotational state J_i. Consequently, the rotational absorption spectrum of such a molecule shows a series of equally spaced lines with a frequency separation of $2B$. Such a spectrum is shown schematically in relation to the allowed energy transitions in Figure 20.4. Because numerous rotational states are populated at room temperature, an actual spectrum has the appearance shown in Figure 20.5.

From gas-phase absorption spectra in these regions, the moment of inertia for the diatomic molecule can be calculated and (because the atomic masses are known) the bond length can be determined.

EXAMPLE 20.1

The microwave absorption spectrum of gaseous NaH (isotope: $^{23}Na^{1}H$) was determined experimentally. The photon wavelength required to excite the molecules rotationally from the state $J = 0$ to $J = 1$ was measured to be 1.02×10^{-3} m. Calculate the bond length of the NaH molecule. Use isotope atomic masses from Table 19.1.

SOLUTION

The reduced mass is

$$\mu = \frac{m_{\text{Na}} m_{\text{H}}}{m_{\text{Na}} + m_{\text{H}}} = \frac{(22.9898\text{ u})(1.0078\text{ u})}{22.9898 + 1.0078\text{ u}}$$

$$= 0.9655\text{ u} = 1.603 \times 10^{-27}\text{ kg}$$

The energy change is

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

which in this case is

$$\Delta E_{\text{rot}} = \frac{(6.626 \times 10^{-34}\text{ J s})(2.998 \times 10^{8}\text{ m s}^{-1})}{1.02 \times 10^{-3}\text{ m}} = 1.95 \times 10^{-22}\text{ J}$$

$$= \frac{h^2}{8\pi^2 I}[(1)(2) - (0)(1)] = \frac{h^2}{4\pi^2 I}$$

Solving for the moment of inertia I gives

$$I = \frac{h^2}{4\pi^2 \Delta E_{\text{rot}}} = \frac{(6.626 \times 10^{-34}\text{ J s})^2}{4\pi^2(1.95 \times 10^{-22}\text{ J})} = 5.70 \times 10^{-47}\text{ kg m}^2$$

The moment of inertia I is related to the bond length R_e by $I = \mu R_e^2$, so

$$R_e^2 = \frac{I}{\mu} = \frac{5.70 \times 10^{-47}\text{ kg m}^2}{1.603 \times 10^{-27}\text{ kg}} = 3.56 \times 10^{-20}\text{ m}^2$$

$$R_e = 1.89 \times 10^{-10}\text{ m} = 1.89\text{ Å}$$

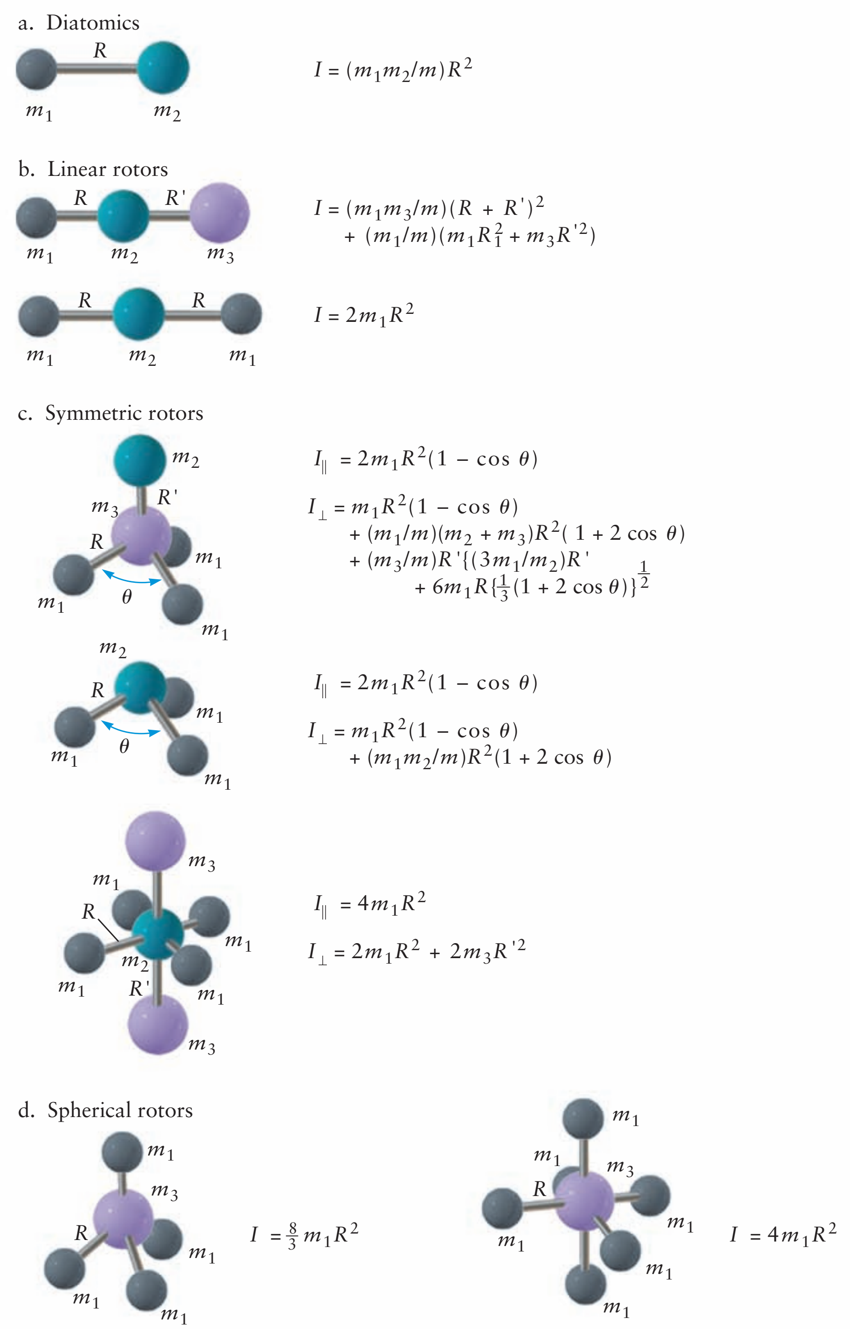
Related Problems: 5, 6, 7, 8

Polyatomic molecules have up to three different moments of inertia, corresponding to rotations about three axes (Fig. 20.6). The rotational spectra for nonlinear polyatomic molecules are more complex than the example just illustrated, but their interpretation is carried out in the same way and has enabled chemists to determine with high accuracy the molecular geometries for many small polyatomic molecules.

Vibrations of Molecules

Now, we give up the restriction that the molecule moves as a rigid body, and we examine its distortions. The information obtained allows us to estimate the "stiffness" of the bond, which is a measure of the bond strength. Figure 20.7 shows the potential energy curve for a diatomic molecule (see also Figs. 3.9 and 6.7). The minimum of the curve corresponds to the equilibrium bond length. The steep rise to the left indicates that the molecule has been "squeezed" to a distance shorter than the equilibrium bond length and repulsive forces are appearing between the two nuclei. The rise to the right indicates that potential energy must be overcome to stretch the bond away from its equilibrium value. The flat region to the extreme right side indicates the amount of energy that must be supplied to dissociate the molecule into free atoms. Consider first the vibrational motion of the diatomic molecule about its equilibrium bond length. If the bond is stretched, the two atoms experience a restoring force that tends to bring them back to their original separation R_e, just as a restoring force acts on the ends of a spring that has been

FIGURE 20.6 Moments of inertia for selected classes of molecular structures. In each case, *m* represents the sum of all the atomic masses in the molecule. (a) Diatomic molecules have a single moment of inertia, uniquely related to the bond length. (b) Linear triatomic molecules also have a single moment of inertia that can be determined from rotational spectra. Because *I* depends on two bond lengths, additional information is required to determine both. This is accomplished by comparing rotational spectra of isotopically substituted molecules. (c) Symmetric rotors have three moments of inertia, of which two are equal. The moment about the vertical *z*-axis through the molecule is called $I_\parallel$ and the two moments about the *x* and *y* axes are called $I_\perp$. The two moments of inertia can be determined from rotational spectroscopy, but additional information (for example from x-ray diffraction) is needed to determine all the bond lengths. (d) Spherical rotors have all three moments of inertia equal. The symmetry of polyatomic molecules guides interpretation of their rotational spectra.
(Adapted from P.W. Atkins, Physical Chemistry (Third Edition), Freeman, 1986.)



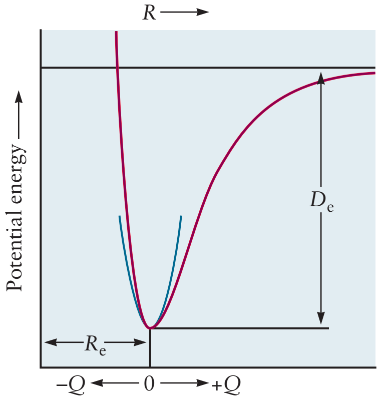


FIGURE 20.7 The potential energy for a diatomic molecule has its minimum at the equilibrium bond length R_e. The displacement coordinate $Q = R - R_e$ represents stretching the bond ($Q > 0$) or compressing the bond ($Q < 0$). For small *Q*, the potential energy is approximated by the harmonic oscillator equation $V(Q) = (1/2)kQ^2$. The bond dissociation energy D_e is defined from the bottom of the potential well at R_e.

stretched. For a small change in bond length $R - R_e$, the force is proportional to that change:

$$F = -k(R - R_e)$$

where the **force constant** k determines the stiffness of the bond. In SI units, k is measured in newtons per meter (Nm^{-1}). The potential energy corresponding to this restoring force is shown as the blue parabolic curve in Figure 20.7.

According to classical mechanics, when a stretched bond is released, the atoms will oscillate back and forth about their average separation, much as two balls connected by a spring do. The oscillation frequency ν is given by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

where μ is again the reduced mass of the harmonic oscillator. In classical mechanics, any vibrational energy is permitted for the oscillator. In quantum mechanics, the Schrödinger equation gives a discrete set of vibrational energy levels (see Section 4.7):

$$E_{\text{vib},n} = (n + \tfrac{1}{2})h\nu \qquad n = 0, 1, 2, \ldots \qquad [20.7]$$

where h is Planck's constant and n is the vibrational quantum number. Note that even in the ground state ($n = 0$) the vibrational energy is not 0. The residual energy $\frac{1}{2}h\nu$ is the **zero-point energy;** it arises from the requirements of the uncertainty principle. Typical energy differences between the ground ($n = 0$) and first excited ($n = 1$) vibrational states range from 2 kJ mol^{-1} to 40 kJ mol^{-1}; they are greater than rotational energy differences but less than electronic energy differences (see Table 20.1). These energy differences correspond to the absorption of radiation in the infrared region of the electromagnetic spectrum, with wavelengths longer than those of visible light. Strong absorption is observed only for transitions between states that differ by 1 in vibrational quantum number ($\Delta n = 1$). Because the separation between adjacent energy levels is independent of quantum number, these energy levels lead to a single vibrational frequency, which can be used to determine the force constant of the bond.

EXAMPLE 20.2

The infrared spectrum of gaseous NaH (isotope: $^{23}\text{Na}^{1}\text{H}$) was determined via absorption spectroscopy. The photon wavelength needed to excite the molecule vibrationally from the state $n = 0$ to $n = 1$ was 8.53×10^{-6} m. Calculate the vibrational force constant of the NaH molecule. Use isotope atomic masses from Table 19.1.

SOLUTION

The vibrational frequency is

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ \text{m s}^{-1}}{8.53 \times 10^{-6}} = 3.515 \times 10^{13}\ \text{s}^{-1} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Solving for the constant k (using the reduced mass from Example 20.1) gives

$$k = \mu(2\pi\nu)^2 = (1.603 \times 10^{-27}\ \text{kg})(2\pi)^2(3.515 \times 10^{13}\ \text{s}^{-1})^2$$
$$= 78.2\ \text{kg s}^{-2} = 78.2\ \text{J m}^{-2}$$

Related Problems: 11, 12, 13, 14

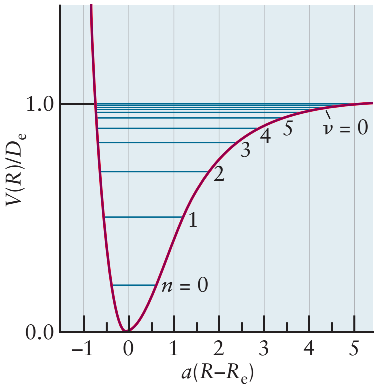


FIGURE 20.8 The Morse potential is defined by $V(R - R_e) = D_e\{1 - \exp[-a(R - R_e)]\}^2$, where $a = (k/2D_e)^{1/2}$. The potential is plotted here in dimensionless variables. Unlike the harmonic oscillator, the Morse potential has a finite number of bound states.

At higher vibrational energies, the motions of the molecule range rather far from the equilibrium value, and they sample the region toward the right side of Figure 20.7, where the motion is said to be "anharmonic." In this case the simple parabolic approximation breaks down, and it is necessary to find the energy levels for the anharmonic potential. Although beyond the scope of this book, this can be carried out for the specific model of the anharmonic potential called the Morse potential (Fig. 20.8). The energy levels are no longer uniformly spaced, and the experimental spectrum shows a progression of frequencies corresponding to these smaller energy gaps. The experimental spectrum can be fit to the Morse potential, and the dissociation energy of the diatomic molecule can be determined.

In a polyatomic molecule, several types of vibrational motion are possible (Fig. 20.9). Each has a different frequency, and each gives rise to a series of allowed quantum vibrational states. Infrared absorption spectra provide useful information about vibrational frequencies and force constants in molecules. For

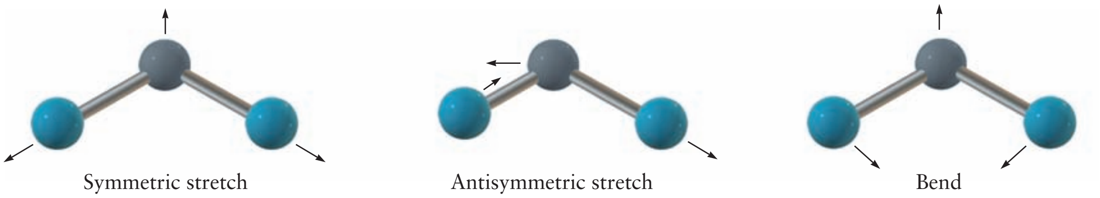


FIGURE 20.9 The three types of vibrational motion that are possible for a bent triatomic molecule. Arrows show the displacement of each atom during each type of vibration.

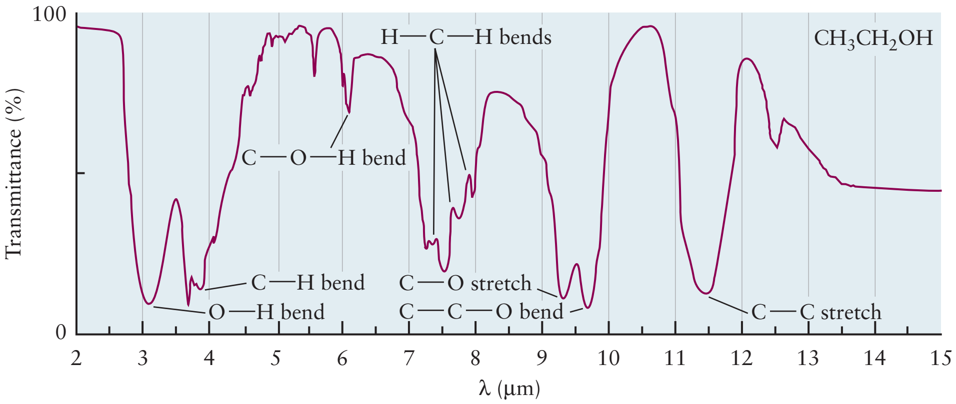


FIGURE 20.10 The infrared absorption spectrum of ethanol, CH_3CH_2OH. Each peak is labeled with the vibrational motion from which it arises.

larger molecules, vibrational spectra are useful for identifying compounds, because each group (such as a C=O bond or a C—OH bond) has its own characteristic frequency in the spectrum, largely independent of the mass, geometry, and other features of the molecule of which it is a part. The spectrum thus provides information about the functional groups in a given molecule (Fig. 20.10).

20.3 Excited Electronic States: Electronic Spectroscopy of Molecules

Excited states of atoms result from the promotion of one or more electrons into orbitals of higher energy. Excited electronic states in molecules arise similarly and can be described in the framework of molecular orbital theory.

As an example, consider the ethylene molecule (C_2H_4). The bonding in ethylene can be described by the combine localized and de-localized method (see Sections 6.5 and 7.3). The two carbon atoms in the molecular "backbone" can be described through sp^2 hybridization. The two remaining carbon $2p_z$ orbitals combined to form a π (bonding) molecular orbital and a π^* (antibonding) molecular orbital for the de-localized electrons. The energy level diagram for the two π orbitals is shown in Figure 20.11. The lowest energy state of ethylene has two electrons in the π orbital. An excited state results when one electron is moved from the π orbital to the π^* orbital. This $\pi \rightarrow \pi^*$ transition in ethylene is caused by absorption of light at the wavelength 162 nm, which lies in the ultraviolet region of the spectrum. An ethylene molecule in this excited state has properties quite different from one in the ground state. The electron in the π^* antibonding orbital cancels the effect of the electron in the π bonding orbital, so the net bond order is reduced from 2 to 1 (the σ bond). Consequently, the molecule in the excited state has a lower bond energy and a longer C—C bond length than in the ground state.

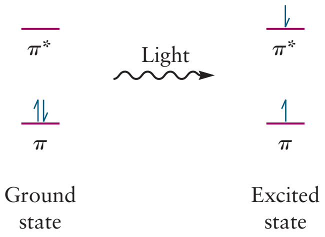


FIGURE 20.11 Occupancy of the π molecular orbitals in the ground state and first excited state of ethylene, C_2H_4. Ethylene in the excited state is produced by irradiation of ground-state ethylene with ultraviolet light in the appropriate frequency range.

Conjugated Systems

Now consider a molecule in which several double bonds alternate with single bonds in a conjugated π-bonding system like that for butadiene. Observe that the lowest energy π orbital in Figure 7.17 extends over the full conjugated π system and resembles a standing wave with a wavelength proportional to the length of the molecule. As more alternating single and double bonds are added, the characteristic wavelengths become longer and the frequencies and energies become lower (Table 20.2). When the chain becomes sufficiently long, the first absorption shifts into the visible region of the spectrum, and the substance takes on color. The color we perceive is related to the absorption spectrum of the material, but only indirectly. What we see is the light transmitted through or reflected from the material, not the light absorbed. So, the color perceived is **complementary** to the color most strongly absorbed by the molecule (Fig. 20.12a and b). Examples are the dyes

TABLE 20.2 Absorption of Light by Molecules with Conjugated π Electron Systems

Molecule	Number of C=C Bonds	Wavelength of Maximum Absorption (nm)
C_2H_4	1	162
C_4H_6	2	217
C_6H_8	3	251
C_8H_{10}	4	304

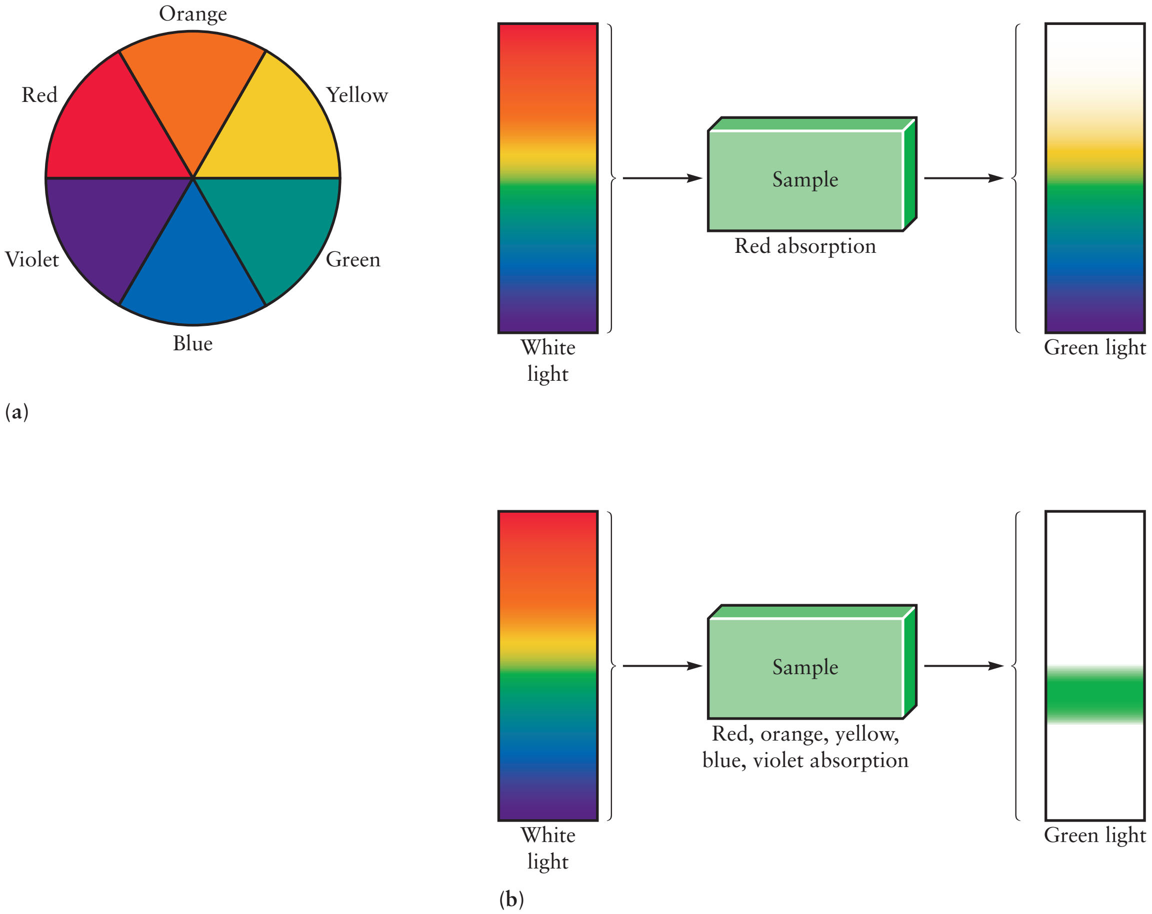


FIGURE 20.12 Two ways in which the color green can be produced. (a) If the sample strongly absorbs red light but transmits yellow and blue light, the sample appears green. (b) If all visible light *except* green is absorbed by the sample, the sample also appears green. The color wheel in (a) shows complementary colors opposite each other.

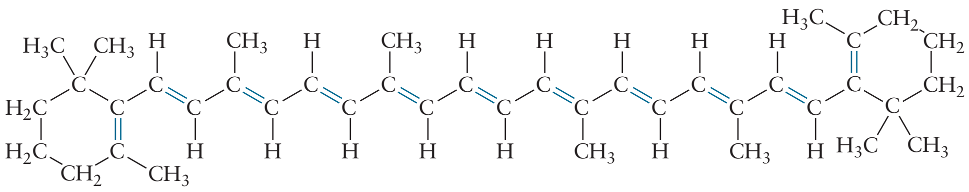


FIGURE 20.13 The molecular structure of the dye beta-carotene. Eleven double bonds alternate with single bonds in this conjugated structure.

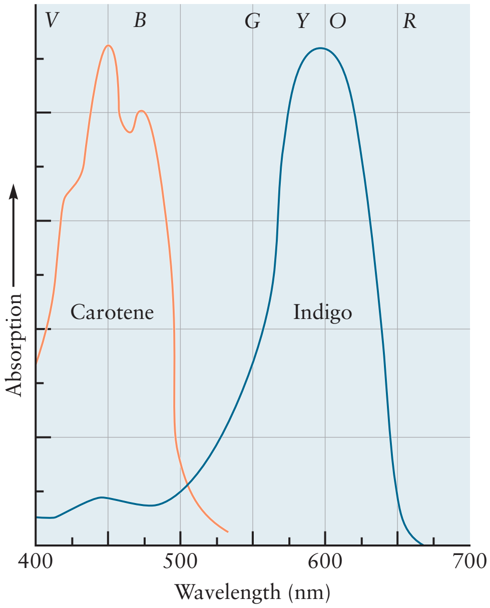


FIGURE 20.14 The absorption spectra of the dyes beta-carotene and indigo differ in the visible region and hence have different colors. The letters stand for the colors of the light at particular wavelengths (violet, blue, green, yellow, orange, and red).

indigo and beta-carotene (Fig. 20.13). Figure 20.14 plots the strength of the absorption of these two dyes at different wavelengths. Indigo absorbs in the yellow-orange region of the spectrum, so it appears violet-blue (the colors complementary to yellow and orange). Beta-carotene absorbs at shorter wavelengths in the blue and violet regions and appears orange or yellow. Indigo is used to dye blue jeans; beta-carotene is responsible for the orange color of carrots, the colors of some processed foods, and the yellow and orange in certain bird feathers.

EXAMPLE 20.3

Suppose you set out to design a new green dye. Over what range of wavelengths would you want your trial compound to absorb light?

SOLUTION

A good green dye must transmit green light and absorb other colors of light. This can be achieved by a molecule that absorbs in the violet-blue *and* orange-red regions of the spectrum (see Fig. 20.12b). Thus, you would want a dye with strong absorptions in both these regions.

The naturally occurring substance chlorophyll, which is responsible for the green colors of grass and leaves, absorbs light over just these wavelength ranges, converting solar energy to chemical energy for the growth of the plant. It is used commercially as a green dye.

Related Problems: 19, 20

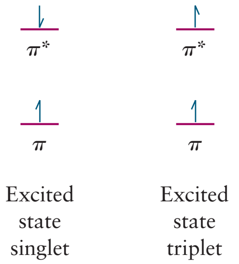


FIGURE 20.15 The first excited singlet and triplet states have the same orbital occupancy but different spin states. The triplet is generally lower in energy.

The Fate of Excited Electronic States

What happens to molecules after they absorb radiation? Some reemit a photon almost immediately and return to the ground electronic state, although they usually end up in rotational and vibrational states different from the original ones. This process is called **fluorescence** and typically occurs within about 10^{-9} s. A second type of light emission called **phosphorescence** occurs much more slowly, over a period of seconds (or in some cases hours). To understand phosphorescence, we have to consider the spins of the electrons in an excited state. The absorption of light (shown in Fig. 20.11) does not change the electron spin and therefore gives an excited state (called a *singlet*) with one spin up and one down. Another possible excited electronic state (called a *triplet*) has both spins up (Fig. 20.15) and, by Hund's rule, has lower energy than the singlet. Although the triplet state cannot be reached directly by absorption of light, there is a small probability that an excited molecule will cross over to the triplet state as it evolves in time or undergoes collisions. Once there, it remains for a long time because emission from a triplet state to a ground singlet state is very slow.

Figure 20.16 schematically illustrates these two pathways for loss of energy by radiation from an electronically excited molecule, along with one nonradiative pathway. In the nonradiative pathway, the molecule may cross over to the ground electronic state and gradually lose its energy as heat to the surroundings as it cascades down to lower vibrational and rotational levels.

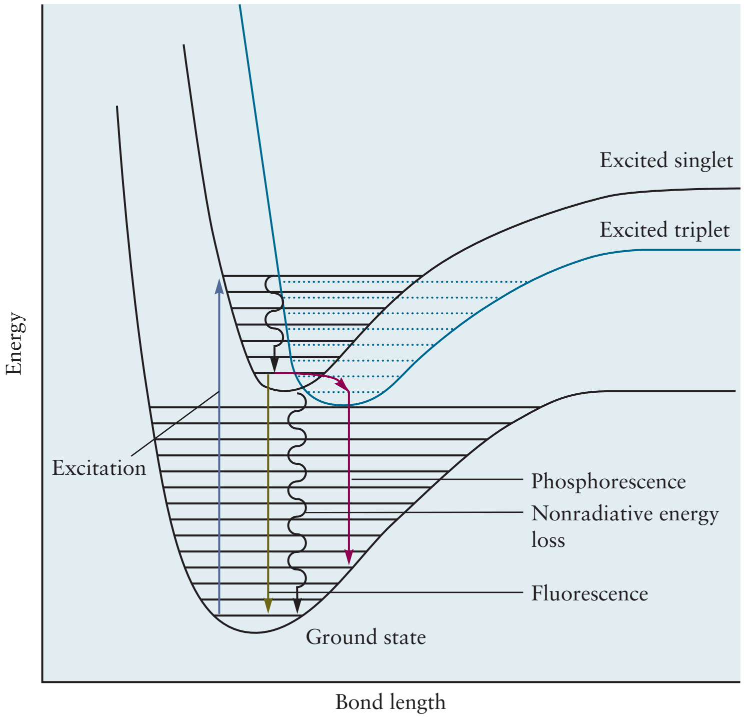
It is possible that the energy of the excited molecule is high enough to break bonds and cause a chemical reaction. Molecules in excited states have enhanced reactivity and can often fragment or rearrange to give new molecules. **Photochemistry,** the study of the chemical reactions that follow the excitation of molecules to higher electronic states through absorption of photons, is an active area of research.

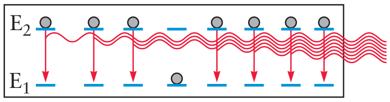
Some compounds are so photochemically sensitive that they must be stored in the dark, because they react rapidly to form products when exposed to light. An example is anhydrous hydrogen peroxide, which reacts explosively in light to give water and oxygen:

$$H_2O_2 \longrightarrow 2\ OH \longrightarrow H_2O + \tfrac{1}{2}O_2$$

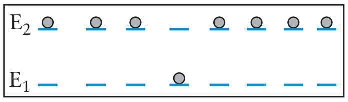
When the energy of a photon of visible light is added to the molecule, the rather weak O—O bond in H_2O_2 breaks apart. This process is called **photodissociation.**

FIGURE 20.16 A schematic picture of the loss of energy by a molecule in an excited electronic state. After the molecule absorbs a photon (purple arrow), it cascades down through a series of levels to the bottom of the excited singlet state (short wavy black arrow). Then three outcomes are possible. The molecule can return to the ground state by fluorescence (green arrow), it can cross over to the triplet state and return from there to the ground state by phosphorescence (red arrow), or it can cross over to the ground state and cascade down without radiating (long wavy black arrow).

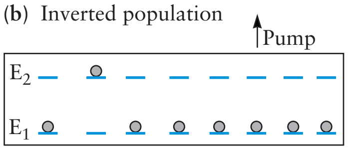




(**c**) Laser action



(**b**) Inverted population



(**a**) Equilibrium population

FIGURE 20.17 Operation of a laser device requires population inversion and stimulated emission.
(Adapted from P.W. Atkins, Physical Chemistry (Third Edition), Freeman, 1986.)

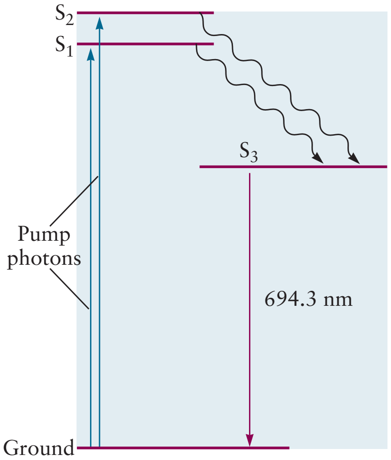


FIGURE 20.18 The ruby laser operates between the ground state and an excited state of Cr^{3+} ions.

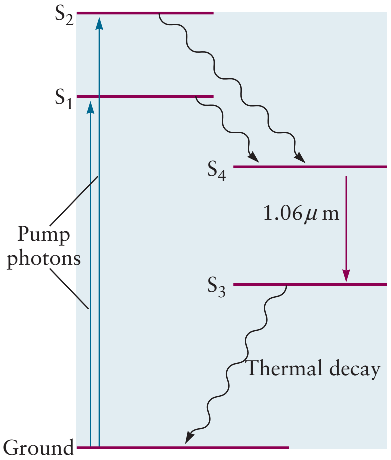


FIGURE 20.19 The neodymium-YAG laser operates between two excited states of the neodymium ions.

Lasers

Through a process called **spontaneous emission,** a molecule or atom in an excited state E_2 can undergo a transition to a lower state E_1 and emit light of frequency $\nu_{12} = (E_2 - E_1)/h$. This radiation will be randomly distributed in phase and in direction; this is "ordinary light." A different process, called **stimulated emission,** can operate between these same two states to emit light of the same frequency ν_{12} but all with a single phase and traveling in a single direction. This is "laser light" whose special properties make it uniquely suited for entertainment functions such as laser light shows and reading information from compact discs (CDs) and digital video discs (DVDs), as well as for a wide range of technical and scientific applications. "**Laser**" is an acronym for **l**ight **a**mplification by **s**timulated **e**mission of **r**adiation.

Suppose we have a material medium containing molecules that have the states E_2 and E_1. Depending on the temperature, molecules will be distributed between these states according to the Boltzmann distribution. Now imagine that we bring a beam of light of frequency ν_{12} into this medium. Whenever the beam hits a molecule in state E_2, the beam will stimulate the excited molecule to emit a new photon of frequency ν_{12}; this increases the intensity of light at frequency ν_{12} in the medium. If we can maintain a so-called "population inversion" in which N_2, the number of molecules in the excited state, is greater than the number N_1 in the lower state and if we can pass this light beam back and forth through the medium many times, then the beam at frequency ν_{12} will be amplified in intensity and will have the special properties of laser light. These are the conditions a practical device must meet to function as a laser.

In Figure 20.17 we sketch the operation of a laser device. The population inversion is achieved by "pumping" in extra energy by thermal excitation, chemical reaction, or optical excitation. The laser medium is contained between two reflecting mirrors that form the "optical cavity" of the laser. When the first few photons are emitted spontaneously from the excited states, they immediately stimulate the emission of more photons. The resulting wave is reflected between the mirrors many times, stimulating further emission on each passage. This growing beam is spatially coherent, meaning that all the waves have the same phase. All the waves are traveling in the same direction, because any wave that might hit one of the mirrors at an angle is reflected out of the pathway and is not amplified. If one of the cavity mirrors is less reflecting than the other, some of the laser light escapes at that end of the cavity and is ready for applications. This phenomenon was first demonstrated by the American physicist Charles Townes at Columbia University using microwave radiation, and the device was called a *maser* (**m**icrowave **a**mplification by **s**timulated **e**mission of **r**adiation).

The first demonstration of laser operation with visible light was achieved in 1960 by the American physicist Theodore Maiman at Hughes Aircraft Research Laboratories in Malibu, California, using the process sketched in Figure 20.18. The laser medium was a rod of ruby (aluminum oxide doped with Cr^{3+} ions), and the laser action occurred between an excited triplet state of the Cr^{3+} ions and their ground state. The population inversion was achieved by optical pumping with a flash lamp to raise ions to the excited singlet state, which then populated the excited triplet state by a radiationless transition. The ruby laser emits visible red light with wavelength 694.3 nm. The chief disadvantage of the ruby laser is that it directly involves the ground state, relative to which it is difficult to maintain a population inversion.

In Figure 20.19 we sketch the operation of the neodymium-YAG laser. The laser medium is a crystal of yttrium-aluminum-garnet doped with neodymium ions. This laser has the advantage over the ruby laser that the laser action occurs between two excited states, and the population inversion is consequently easier to maintain. The Nd-YAG laser is widely used in science and technology. One major application is to pump the so-called "dye lasers" in which the medium is intensely colored dye molecules (usually with conjugated double bonds) dissolved in

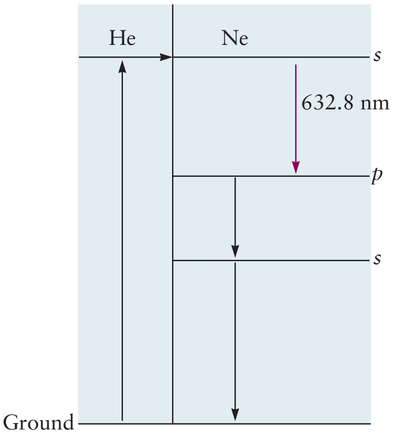


FIGURE 20.20 The He-Ne laser emits from an excited state of the Ne atom, which is produced by collisions with He atoms excited in an electrical discharge.

methanol. Dye lasers are "tunable," which means that laser light can be obtained over essentially the entire visible wavelength range. Pumped dye lasers are widely used in research on molecular spectroscopy and energy transfer processes.

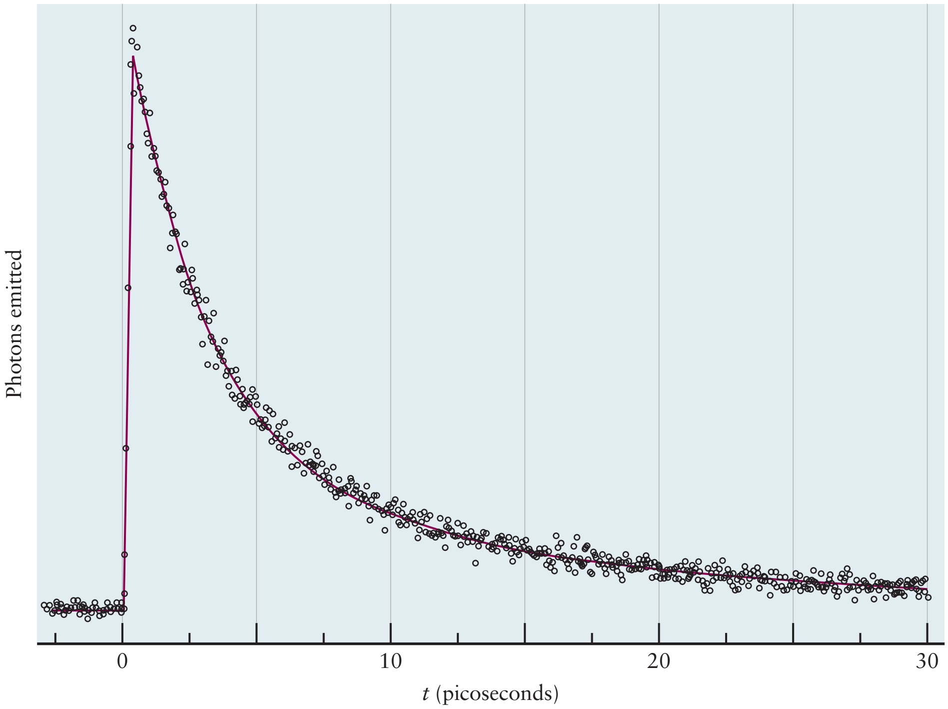
In Figure 20.20 we sketch operation of the He-Ne laser, which provides the red laser light widely used in applications such as alignment of mechanical tools and intruder detection systems. The light is emitted with wavelength 632.8 nm between two states in excited Ne atoms. The pumping process relies first on excitation of He atoms by collisions with energetic electrons in an electrical discharge. This excitation level happens to coincide with an excited state of Ne, and the excitation is transferred from He to Ne during a collision. This gives a number of Ne atoms in highly excited states, and the laser action occurs during a transition to an unpopulated state above the ground state.

Lasers for CDs and DVDs are based on emission from solid state semiconductor materials; their operation is described in Chapter 22.

Newer Methods in Spectroscopy

All the spectroscopy methods described up to this point are carried out in the manner shown in Figure 20.2. They identify transitions between energy levels of molecules, from which we extract information about molecular structure and bonding. Modern molecular spectroscopy aims to go further and give us an understanding of the dynamics of excited molecules—a detailed series of events that may include nuclear motion, light emission, and electron transfer. Such an understanding requires **time-resolved spectroscopy,** in which short light pulses excite molecules and the emitted photons are identified not only by wavelength but also by the time delay from the exciting pulse until the appearance of each photon. Light pulses with durations of picoseconds (10^{-12} s) and even femtoseconds (10^{-15} s) can be generated by modern lasers. The very rapid evolution of excited molecules is monitored by measuring their absorption of a second light pulse—which arrives at a variable time after the initial pulse—or by counting photons emitted by the excited molecules as a function of time (Fig. 20.21).

A promising approach to simplifying the spectra of complex molecules relies upon cooling the molecules in a special type of molecular beam called the



Courtesy of Prof. Graham Fleming, University of California, Berkeley

FIGURE 20.21 The initial chemical step in photosynthesis, as carried out by the purple bacterium *R. sphaeroides,* is the transfer of an electron from the excited state of a pair of chlorophyll molecules to a pheophytin molecule located 17 Å away. (Section 20.6 describes the structure of the reaction center in greater detail.) This electron transfer occurs very rapidly and with essentially 100% efficiency. Ultrafast spectroscopy monitors the electron transfer by detecting the disappearance of the excited state of the pair of chlorophyll molecules through the decay of its fluorescence. The data shown here reveal that the electron moves to the pheophytin with a half-life of 2.8 picoseconds (2.8×10^{-12} s).

supersonic jet. A typical, moderate-size molecule in solution has a rather broad and featureless spectrum in the visible and ultraviolet regions (Fig. 20.22, red curve). The dissolved molecule has numerous vibrational and rotational levels. Interactions between the dissolved molecule and solvent molecules at different distances shift these vibrational and rotational energies, giving a blurred overall picture of the spectrum. (The same blurring of rotational levels within a particular vibrational state causes the broad bands in Fig. 20.10.) When a molecule is vaporized into the gas state, the effects of solvent are removed and additional structure appears in its spectrum (see Fig. 20.22, blue curve). Even so, molecular collisions and the numerous thermally occupied vibrational and rotational energy levels still give bands that are too broad to be interpreted quantitatively. To simplify the spectrum even further, it would help to cool the molecule to low temperatures so that very few levels are occupied. But then the gas would then condense to a liquid or solid and defeat the purpose of isolating the molecules. The supersonic jet molecular beam apparatus solves the problem by cooling and isolating the molecules. In a supersonic jet, the molecules to be studied—along with a carrier gas such as helium—are forced through a nozzle into a vacuum at supersonic speeds. The gas expands adiabatically, which cools the molecules (see Section 12.6). Collisions redistribute molecules into lower energy levels, until downstream in the jet the effective temperatures are quite low. As the beam expands into the vacuum, collisions cease, and the cooled molecules fly along in isolation. Under these conditions much more detailed structure appears in the spectra (see Fig. 20.22, inset).

Surprising as it may seem, another way to simplify spectra is to examine one molecule at a time. Chemists have studied the spectra of molecules present in low concentrations in a low-temperature solid. Working with thin samples and

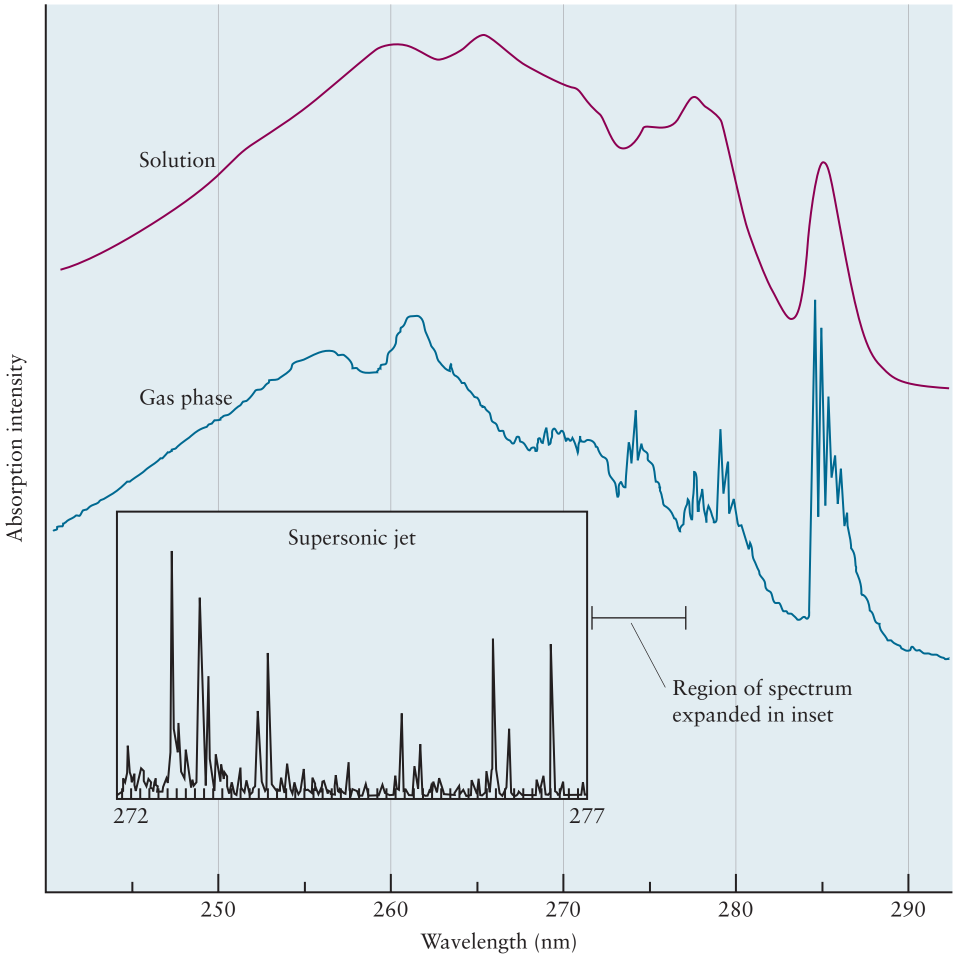


FIGURE 20.22 A portion of the absorption spectrum of indole, C_8H_7N, in the ultraviolet region. In heptane solution (red curve) the spectrum has broad and featureless bands, whereas in the gas phase (blue curve) additional structure appears. Cooling indole molecules in a supersonic jet reveals a large number of sharp absorption lines (see inset, which covers a very small range of wavelengths).

Courtesy of Prof. Donald Levy and Dr. H. Strickland, The University of Chicago

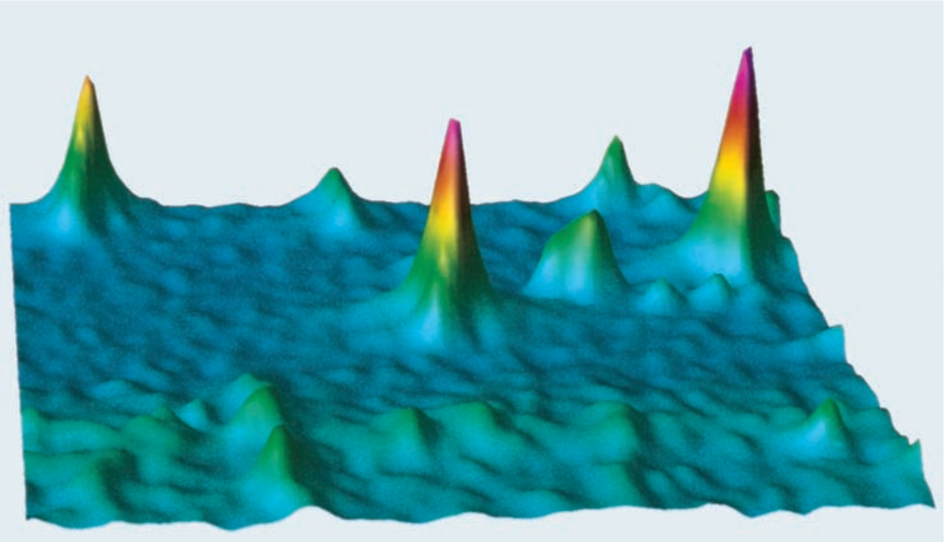


FIGURE 20.23 Images of the fluorescence of single molecules. The height of each peak gives the intensity of light emitted by that molecule. The axis into the page is spatial position (scanned over a distance of 4 × 1^{-5} m), and the horizontal axis scans a narrow range of wavelengths for the exciting light.

Courtesy of Prof. W. E. Moerner, Stanford University

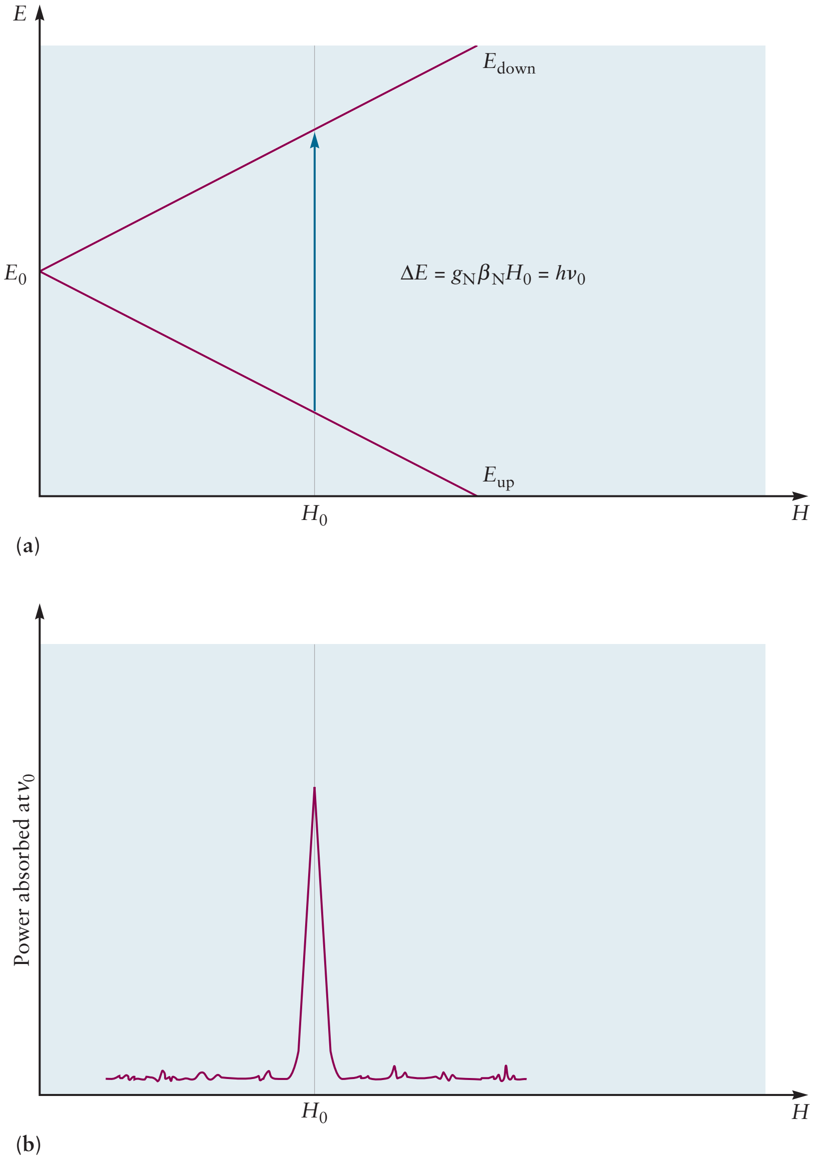
focused laser beams, they can probe a region of the sample with a relatively small number of those molecules. Using extraordinarily sensitive detectors, they measure signals from one molecule at a time (Fig. 20.23). Chemists can even see how a signal changes with time; as the molecules near the probed molecule move, the frequencies of transitions in the probed molecule shift as well. Thus, chemists not only can "see" single atoms with scanning tunneling microscopes (see Fig. 1.12), they can also probe the spectra of single molecules.

20.4 Nuclear Magnetic Resonance Spectroscopy

Just as electrons have spin, so do some nuclei have spins, and the energies of their different spin states are split apart by a magnetic field. Hydrogen (^{1}H) nuclei have "spin-up" and "spin-down" states in which the proton behaves as if it were a tiny bar magnet. In a magnetic field the protons with spin up align parallel to the field (lower energy configuration), and those with spin down align antiparallel to the field (higher energy configuration). The analogy with bar magnets suggests the difference in energy between these two states will be determined by the strength of the magnetic field H. The magnitude of the energy splitting is $\Delta E = g_N \beta_N H$ where g_N is the "nuclear g-factor" for protons and β_N is a constant called the nuclear magneton (Fig. 20.24). These nuclei can change spin state by absorbing or emitting photons of magnitude $h\nu = g_N \beta_N H$, which fall in the FM radio frequency (rf) region of the electromagnetic spectrum. In nuclear magnetic resonance (NMR) spectroscopy, low-energy radio waves (photons carrying energies between 0.00002 kJ mol^{-1} and 0.00020 kJ mol^{-1}) "tickle" the nuclei in a molecule, and cause spin transitions.

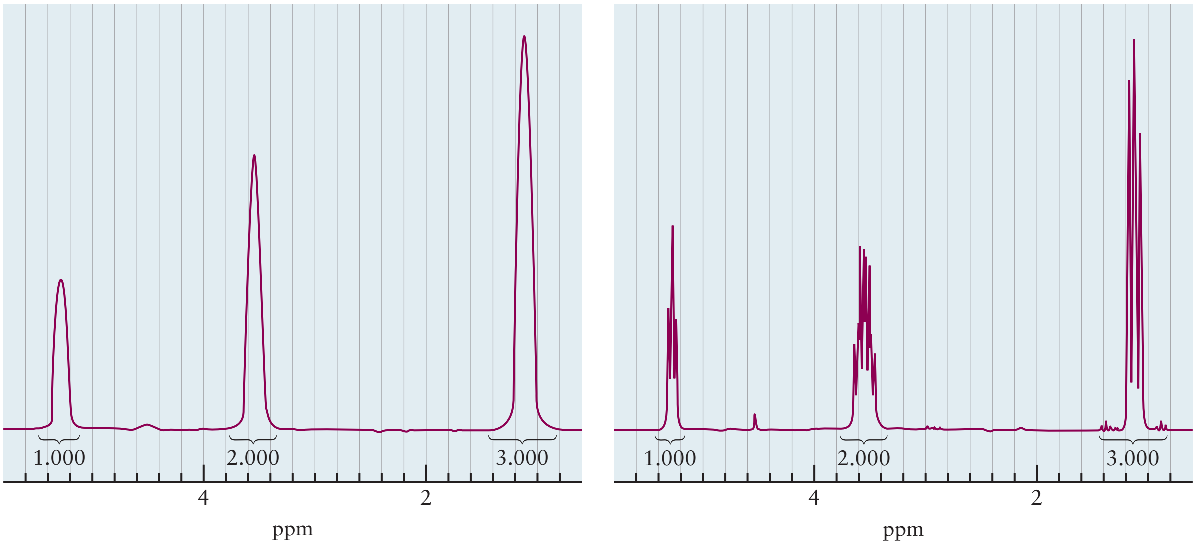
The NMR spectrum can be recorded in various ways. The earliest commercial NMR spectrometers operated in continuous-wave mode, in which the sample is irradiated at constant frequency ν while the magnetic field is swept through a range of values. The rf power absorbed by the sample is recorded at each value of H. When the value of H satisfies the resonance condition, a peak appears in the spectrum. Newer instruments rely on **Fourier transform (FT NMR) spectroscopy,** in which a sample held in a fixed magnetic field is irradiated with a short, intense burst of

FIGURE 20.24 (a) Energy-level diagram for proton NMR measurements. The magnitude of the energy gap between the spin states depends on the strength of the applied magnetic field. (b) Energy is absorbed when the magnetic field and the rf radiation satisfy the resonance condition.



rf power spanning a frequency range broad enough to stimulate many transitions. The specific frequencies of all the many transitions are measured simultaneously and stored in computer memory. A complete spectrum can be acquired within a few seconds. The measurement can be repeated many times and the results averaged in computer memory to reduce the effects of random background noise. FT NMR spectrometers detect numerous nuclei besides ^{1}H (^{13}C holds special interest in organic chemistry and biochemistry), but our discussion is limited to ^{1}H.

Nuclear spins are sensitive to the chemical environment of a nucleus. Electrons moving near the nucleus establish an internal magnetic field that modifies the local effective field felt by each proton to a value different from that of the externally applied field. The resulting **chemical shift** causes protons within different structural units of the molecule to show NMR peaks at different values of magnetic field. All protons in chemically equivalent environments will contribute to a single absorption peak in the spectrum. The relative area under each absorption peak is proportional to the number of protons within each equivalent group. In order to standardize procedures, chemical shift values are recorded relative to the selected reference compound tetramethylsilane (TMS) by adding a very small amount of



(a) (b)

Courtesy of Dr. Jane Strouse, UCLA

FIGURE 20.25 Proton NMR spectrum for ethanol. (a) The low-resolution spectrum shows a single broad peak for each chemically equivalent group of protons. (b) In high resolution, spin-spin splitting separates the peak for each chemically equivalent group of protons into a multiplet. The relative area under each peak, which is proportional to the number of protons responsible for the peak, is given by the number under the brackets below each peak.

FIGURE 20.26 A magnetic resonance imaging (MRI) machine. The patient lies underneath the magnet opening.
(© Mauro Fermariello/Science Photo Library/Photo Researchers, Inc.)

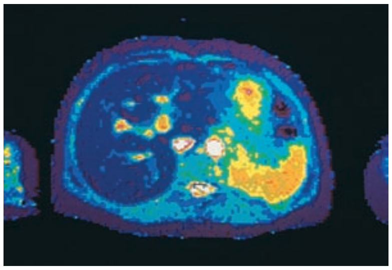


FIGURE 20.27 An MRI scan of the abdomen of a healthy person. The liver is the large blue mass (top and left); the spleen is at the lower right (yellow). Stomach contents are at the top right (red and yellow). The purple outer layer is fat.
(© Alexander Tsiaris/Science Source/Photo Researchers, Inc.)

TMS to the sample. The chemical shift for each proton in the spectrum is then defined in units of parts per million (ppm) as

$$\delta = \frac{H_s - H_r}{H_r} \times 10^6 \qquad [20.8]$$

where H_s is the value of the magnetic field at the peak in the sample spectrum and H_r is the value at the TMS peak. Extensive tables of chemical shift values relative to TMS aid the interpretation of spectra. For example, these considerations predict that the NMR spectrum of ethanol, $CH_3{-}CH_2{-}OH$ should have three peaks of relative area 3:2:1. This is exactly the result obtained when the spectrum is acquired with low resolution (Fig. 20.25a).

Nuclear spins are also sensitive to other nearby nuclear spins. Because each spin behaves as if it were a small bar magnet, each influences the local value of magnetic field felt by others nearby. The result is **spin–spin splitting,** which breaks the broad peak of each chemically equivalent group of protons into a multiplet of narrower, sharper peaks. So long as the chemical shift between chemically nonequivalent groups of protons is large, the multiplet patterns can be interpreted by qualitative rules that we do not describe here. For example, when applied to ethanol, these rules predict splitting of the CH_3 protons into a triplet and splitting of the CH_2 protons into a quartet, as seen in high-resolution experimental spectra (see Fig. 20.25b). Through chemical shifts and spin-spin splitting, nuclear magnetic resonance spectroscopy offers a way to identify the bonding groups in a molecule and interpret molecular structure.

An adaptation of NMR spectroscopy used in medical diagnosis is called **magnetic resonance imaging (MRI).** It relies on emission by the protons in the water contained in the organs of the body. The patient is placed under the opening of a large magnet (Fig. 20.26), and a radio transmitter raises the proton spins in the relevant part of the body to their high-energy state. The rf photons subsequently emitted are then detected by a radio receiver coil. The amplitude of the signal indicates the excess or deficiency of water present. Thus, MRI can identify tumors by the excess water in their cells. The time delay until emission occurs is related to the type of tissue being examined. Figure 20.27 shows an MRI scan of the abdomen.

20.5 Introduction to Atmospheric Photochemistry

In photosynthesis, green plants and photosynthetic bacteria harvest energy from the sun through photochemical reactions. The ability of light to cause chemical reactions is also apparent in the earth's atmosphere. In fact, photosynthesis and atmospheric chemistry are intimately connected. Reactions in the atmosphere determine the intensities and wavelengths of light that reach the earth's surface to be harvested by living species. At the same time, oxygen, the gas produced by green-plant photosynthesis, has transformed the atmosphere; before photosynthesis began, there was almost no free oxygen at the earth's surface.

Although the chemical composition summarized in Table 9.1 describes the average makeup of the portion of the atmosphere closest to the earth's surface, it does not do justice to the variation in chemical properties with altitude, to the dramatic role of local fluctuations in trace gases, or to the dynamics underlying observed average concentrations. The atmosphere is a complex chemical system that is far from equilibrium. Its properties are determined by an intricate interplay of thermodynamic and kinetic factors. It is a multilayered structure, bathed in radiation from the sun and interacting at the bottom with the oceans and land masses. At least four layers are identifiable, each with a characteristic variation of temperature (Fig. 20.28). In the outer two layers (the **thermosphere** and the **mesosphere**), atmospheric density is low and the intense radiation from the sun causes extensive ionization of the particles that are present. The third layer, the **stratosphere,** is the region from 12 km to 50 km (approximately) above the earth's surface. The **troposphere** is the lowest region, extending 12 km out from the earth's surface. In the troposphere, warmer air lies beneath cooler air. This is a dynamically unstable situation because warm air is less dense and tends to rise, so convection takes place, mixing the gases in the troposphere and determining the

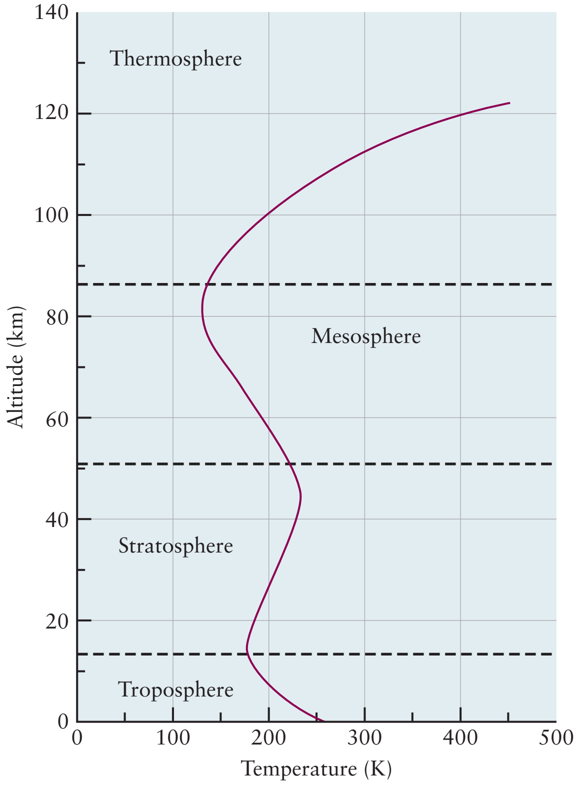


FIGURE 20.28 The variation of the temperature of the atmosphere with altitude, showing the layered structure of the atmosphere.

weather. In the stratosphere the temperature increases with altitude and there is little vertical mixing from convection. Mixing across the borders between the layers is also slow, so most chemical processes in each layer can be described separately.

Research in atmospheric chemistry dates back to the 18th century. Cavendish, Priestley, Lavoisier, and Ramsay were the first scientists to study the composition of the atmosphere. In recent years, atmospheric chemistry has developed in two different but related directions. First, the sensitivity of chemical analysis has greatly improved, and analyses for substances at concentrations below the part-per-billion (ppb) level are now carried out routinely. Airplanes and satellites enable scientists to map the global distributions of trace substances. Second, advances in gas-phase chemical kinetics have led to a better quantitative understanding of the ways in which substances in the atmosphere react with one another and with light. Much of the impetus for these studies of atmospheric chemistry comes from concern about the effect of air pollution on life.

Stratospheric Chemistry

As Figure 4.6 shows, the sun emits light over a broad range of wavelengths, with the highest intensity at about 500 nm, in the visible region of the spectrum. The intensities at wavelengths down to 100 nm in the ultraviolet region are quite substantial, and because the energy $h\nu$ carried by a photon is inversely proportional to the wavelength $\lambda(h\nu = hc/\lambda)$, the ultraviolet photons carry much more energy than do photons of visible light. If these photons could penetrate to the earth's surface in substantial numbers, they could greatly damage living organisms. The outer portions of the atmosphere (especially the thermosphere) play a crucial role in preventing this penetration through the photodissociation of oxygen molecules:

$$O_2 + h\nu \longrightarrow 2O$$

where $h\nu$ symbolizes a photon. This reaction reduces the number of high-energy photons reaching the lower parts of the atmosphere, especially those with wavelengths less than 200 nm.

EXAMPLE 20.4

The bond dissociation energy of O_2 is 496 kJ mol^{-1}. Calculate the maximum wavelength of light that can photodissociate an oxygen molecule.

SOLUTION

Because 496 kJ dissociates 1.00 mol of O_2 molecules, the energy to dissociate one molecule is found by dividing by Avogadro's number:

$$\frac{496 \times 10^3 \text{ J mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 8.24 \times 10^{-19} \text{ J}$$

A photon carrying this energy has a wavelength λ, given by

$$8.24 \times 10^{-19} \text{ J} = h\nu = \frac{hc}{\lambda}$$

so

$$\lambda = \frac{hc}{8.24 \times 10^{-19} \text{ J}} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{8.24 \times 10^{-19} \text{ J}}$$

$$= 2.41 \times 10^{-7} \text{ m} = 241 \text{ nm}$$

Any photons with wavelengths *shorter* than this are energetic enough to dissociate oxygen molecules. Those with wavelengths shorter than 200 nm are the most efficient in causing photodissociation.

Related Problems: 29, 30

Rather few photons with wavelengths below 200 nm can penetrate to the stratosphere, but those that do establish a small concentration of oxygen atoms in that layer. These atoms can collide with the much more prevalent oxygen molecules to form highly excited molecules of ozone, symbolized by O_3^*:

$$O + O_2 \rightleftarrows O_3^*$$

The excited-state O_3^* can dissociate in a unimolecular reaction back to O and O_2, as indicated by the reverse arrow in this equilibrium. Alternatively, if another atom or molecule collides with it soon enough, some of its excess energy can be transferred to that atom or molecule. This process is represented as

$$O_3^* + M \longrightarrow O_3 + M$$

where M stands for the atom or molecule with which the O_3^* collides. The most likely candidates for M are oxygen and nitrogen molecules, because they are the most abundant species in the atmosphere. The net effect of these two reactions is to produce a small concentration of ozone in the stratosphere.

Under laboratory conditions, ozone is an unstable compound. Its conversion to oxygen is thermodynamically spontaneous

$$O_3(g) \longrightarrow \tfrac{3}{2}\,O_2(g) \qquad \Delta G° = -163 \text{ kJ}$$

but the rate is quite slow in the absence of light. In the stratosphere, ozone photodissociates readily to O_2 and O in a reaction that requires about 106 kJ per mole of ozone, much less than that required for the dissociation of O_2:

$$O_3 + h\nu \longrightarrow O_2 + O$$

This process occurs most efficiently for wavelengths between 200 and 350 nm. The energy of light in this range of wavelengths is too small to be absorbed by molecular oxygen but large enough to damage organisms at the earth's surface. The ozone layer shields the earth's surface from 200-nm to 350-nm ultraviolet radiation coming from the sun. The balance between formation and photodissociation leads to a steady-state concentration of more than 10^{15} molecules of ozone per liter in the stratosphere.

It is important to know whether molecules being released in the lower atmosphere can reach the stratosphere and affect the amount of ozone in it. Certain types of air pollution give rise to **radicals** that catalyze ozone depletion. A radical is a chemical species that contains an odd (unpaired) electron, and it is usually formed by the rupture of a covalent bond to form a pair of neutral species. One pressing concern involves chlorofluorocarbons (CFCs)—compounds of chlorine, fluorine, and carbon used as refrigerants and as propellants in some aerosol sprays. CFCs are nonreactive at sea level but can photodissociate in the stratosphere:

$$CCl_2F_2 + h\nu \longrightarrow CClF_2 + Cl$$

The atomic chlorine released thereby soon reacts with O atoms or O_3 to give ClO:

$$Cl + O \longrightarrow ClO$$

$$Cl + O_3 \longrightarrow ClO + O_2$$

The ClO radical is the immediate culprit in the destruction of stratospheric ozone. Local increases in ClO concentration are directly correlated with decreases in O_3 concentration. ClO catalyzes the destruction of ozone, probably by the mechanism

$$\begin{aligned}
2\,\mathrm{ClO} + \mathrm{M} &\longrightarrow \mathrm{ClOOCl} + \mathrm{M} \\
\mathrm{ClOOCl} + h\nu &\longrightarrow \mathrm{ClOO} + \mathrm{Cl} \\
\mathrm{ClOO} + \mathrm{M} &\longrightarrow \mathrm{Cl} + \mathrm{O_2} + \mathrm{M} \\
2 \times (\mathrm{Cl} + \mathrm{O_3} &\longrightarrow \mathrm{ClO} + \mathrm{O_2}) \\
\hline
\text{net reaction: } 2\,\mathrm{O_3} &\longrightarrow 3\,\mathrm{O_2}
\end{aligned}$$

where M stands for N_2 and O_2 molecules. This catalytic cycle is ordinarily disrupted rather quickly as Cl reacts with other stratospheric species to form less reactive "reservoir molecules" such as HCl and $ClONO_2$. But, the lack of mixing in the stratosphere keeps the reservoir molecules around for long periods.

It is believed that atomic Cl escapes its reservoir molecules through heterogeneous reactions on the polar stratospheric clouds that form during the intense Antarctic winter. The liberated Cl gives rise to the annual "ozone holes" above the Antarctic. During these episodes, more than 70% of the total column ozone is depleted before the values rise again (Fig. 20.29). Researchers have demonstrated that the extent of depletion above the Antarctic increases each year (Fig. 20.30), and measurements have shown smaller but still serious depletions over other parts of the globe. International agreement (the Montreal Protocol) banned the production of cholorfluorocarbons by industrialized nations by the end of the 20th century. Developing countries have until 2010 to comply with the regulation.

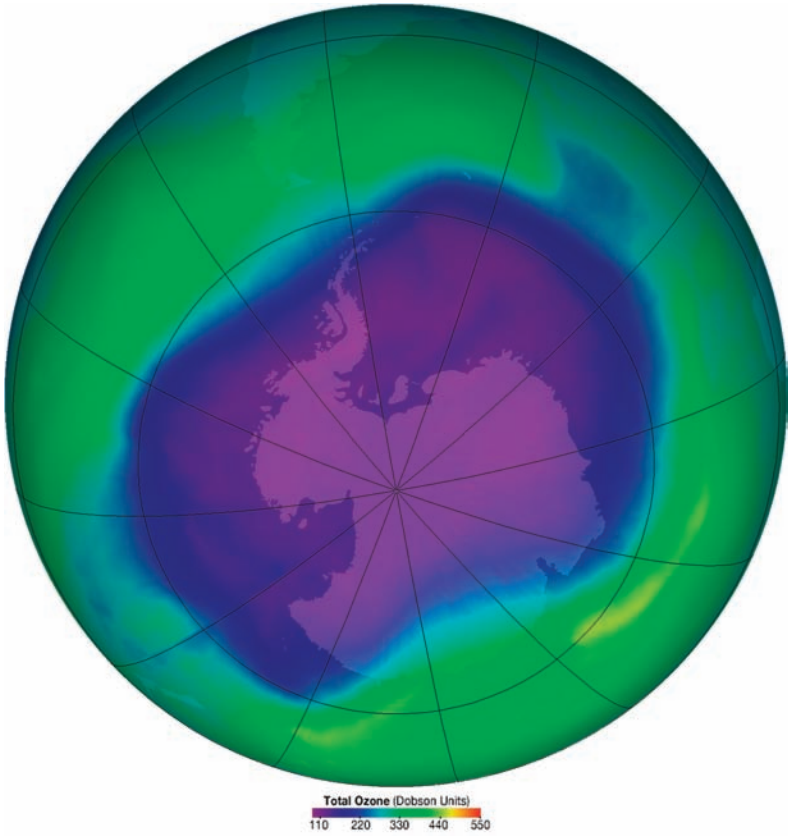


FIGURE 20.29 This false color image shows total stratospheric ozone amounts over the southern hemisphere for September 24, 2006, as recorded by the Ozone Monitoring Instrument (OMI) mounted on the Aura spacecraft. The dramatic depletion of the ozone layer over Antarctica is revealed with the help of the false color scale at the bottom of the figure. Ozone amounts are commonly expressed in Dobson units; 300 Dobson units is a typical global average over the course of a year. The size of the Antarctic ozone hole was near a record high and the levels of ozone near a record low on this date.

NASA

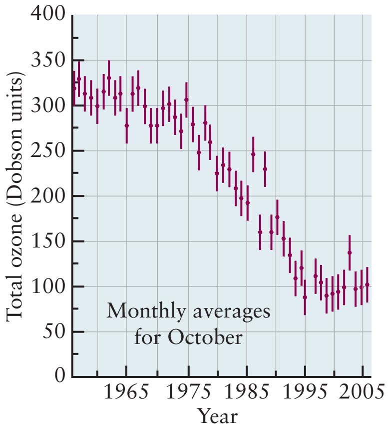


FIGURE 20.30 Worsening ozone depletion over Halley Bay, Antarctica. These measurements were all taken in the Antarctic spring (October) when depletion is at its worst.

Tropospheric Chemistry

The troposphere is the part of the atmosphere in contact with the earth's surface. It is therefore most directly and immediately influenced by human activities, especially by the gases or small particles put into the air by automobiles, power plants, and factories. Some pollutants have long lifetimes and are spread fairly evenly over the earth's surface; others attain large concentrations only around particular cities or industrial areas.

The oxides of nitrogen are major air pollutants. Their persistence in the atmosphere demonstrates the importance of kinetics, as opposed to thermodynamics, in the chemistry of the atmosphere. All of the oxides of nitrogen are thermodynamically unstable with respect to the elements at 25°C, as shown by their positive free energies of formation. They form whenever air is heated to high enough temperatures, either in an industrial process or in the engine of a car. They accumulate to build up concentrations much higher than the equilibrium values because they decompose slowly. The interconversion among NO, NO_2, and N_2O_4 is rapid and strongly temperature-dependent, so they are generally grouped together as "NO_x" in pollution reports. Photochemical smog is formed by the action of light on nitrogen dioxide, followed by reaction to produce ozone:

$$NO_2 + h\nu \longrightarrow NO + O$$

$$O + O_2 + M \longrightarrow O_3 + M \qquad (M = N_2 \text{ or } O_2)$$

It may seem paradoxical that concern about ozone in the stratosphere involves its potential *depletion,* whereas concern about the troposphere involves the *production* of ozone. Although ozone is beneficial in preventing radiation from penetrating to the earth's surface, it is quite harmful in direct contact with organisms because of its strong oxidizing power. Levels of 10 ppm to 15 ppm are sufficient to kill small mammals, and a concentration as low as 3 ppm is enough to trigger an "ozone alert." In addition, ozone reacts with incompletely oxidized organic compounds from gasoline and with nitrogen oxides in the air to produce harmful irritants such as methyl nitrate (CH_3NO_3).

The oxides of sulfur create global pollution problems because they have longer lifetimes in the atmosphere than the oxides of nitrogen. Some of the SO_2 and SO_3 in the air originates from biological processes and from volcanoes, but much comes from the oxidation of sulfur in petroleum and in coal burned for fuel. If the sulfur is not removed from the fuel or the exhaust gas, SO_2 enters the atmosphere as a stable but reactive pollutant. Further oxidation by radicals leads to sulfur trioxide:

$$SO_2 + OH \longrightarrow SO_2OH$$

$$SO_2OH + O_2 \longrightarrow SO_3 + OOH$$

$$OOH \longrightarrow O + OH$$

The atomic oxygen thus produced can react with molecular oxygen to form ozone. **Acid rain** results from the reaction of NO_2 and SO_3 with hydroxyl radical and water vapor in the air to form nitric acid (HNO_3) and sulfuric acid (H_2SO_4). The acids dissolve in water and return to the earth in the rain.

The Greenhouse Effect

As we have seen, most of the short-wavelength photons from the sun are absorbed by the outer atmosphere and do not reach the earth's surface. The radiation that does reach the earth is in steady state balance with re-radiation into space, which helps to maintain a livable temperature. Certain gases in the troposphere play a crucial role in this balance because they absorb infrared radiation emitted by the warm surface of the earth rather than letting it pass out to space (Fig. 20.31). In

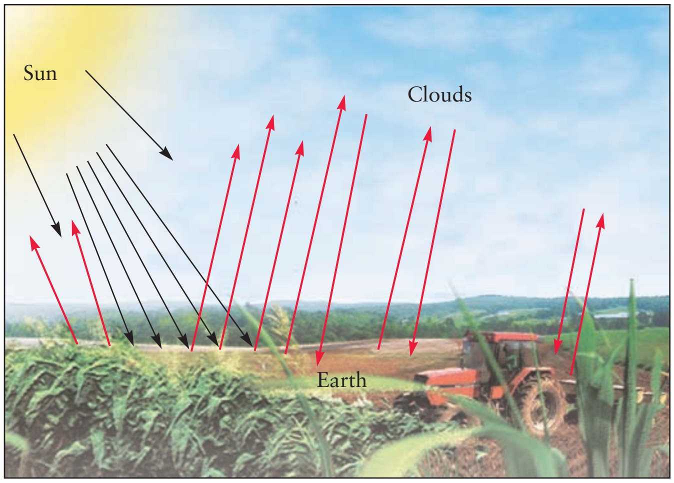


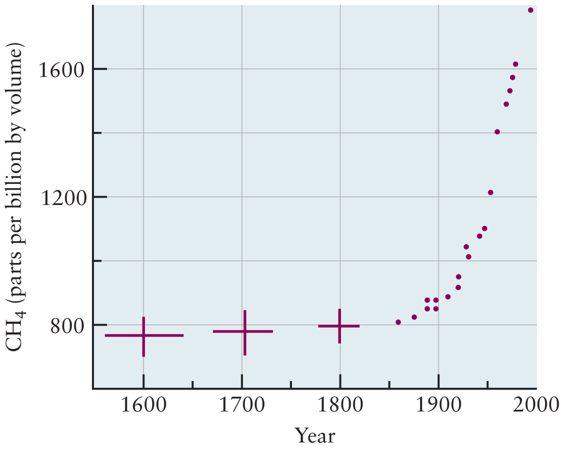
FIGURE 20.31 Visible light from the sun strikes the earth's surface and heats it. Much energy is radiated back into space in the longer wavelength infrared region of the spectrum. Molecules in the atmosphere and in clouds can block some of this loss, keeping the lower atmosphere warmer than it would be without these molecules.

winter, the temperature does not fall as low on cloudy nights as on clear nights because the water vapor in the clouds provides a thermal blanket, absorbing outgoing radiation with wavelengths near 2×10^{-5} m and reradiating it to the earth's surface.

Two other gases that absorb infrared radiation to a significant extent are carbon dioxide and methane. Both are uniformly distributed in fairly low concentrations through the troposphere, but their concentrations have increased steadily over the 200 to 300 years since the beginning of the industrial revolution (Fig. 20.32). The tremendous increase in the burning of fossil fuels for energy is a major contributor to the increase of CO_2 (Fig. 20.33). It is estimated that by the year 2050 the concentration of CO_2 in the atmosphere will be double the premodern value. Chlorofluorocarbons also absorb infrared radiation, especially over some key wavelength ranges left open by CO_2 and water vapor.

Such changes are viewed with alarm because of a phenomenon called the **greenhouse effect.** This term refers to a global increase in average surface temperature of the earth's surface that occurs when heat given off at the earth's surface is prevented from escaping into space by gases that absorb and reradiate infrared radiation. An increase in average surface temperature of 2°C to 5°C over the next century would have major consequences, including melting some polar ice—and a consequent rise in the level of the oceans—and the conversion of arable land to desert. To prevent these undesirable changes, it will be necessary in the next decades to develop new energy sources not based on burning fossil fuels.

FIGURE 20.32 The concentration of methane in the lower atmosphere has doubled since 1600. Note the dramatic increase in the last 100 years.



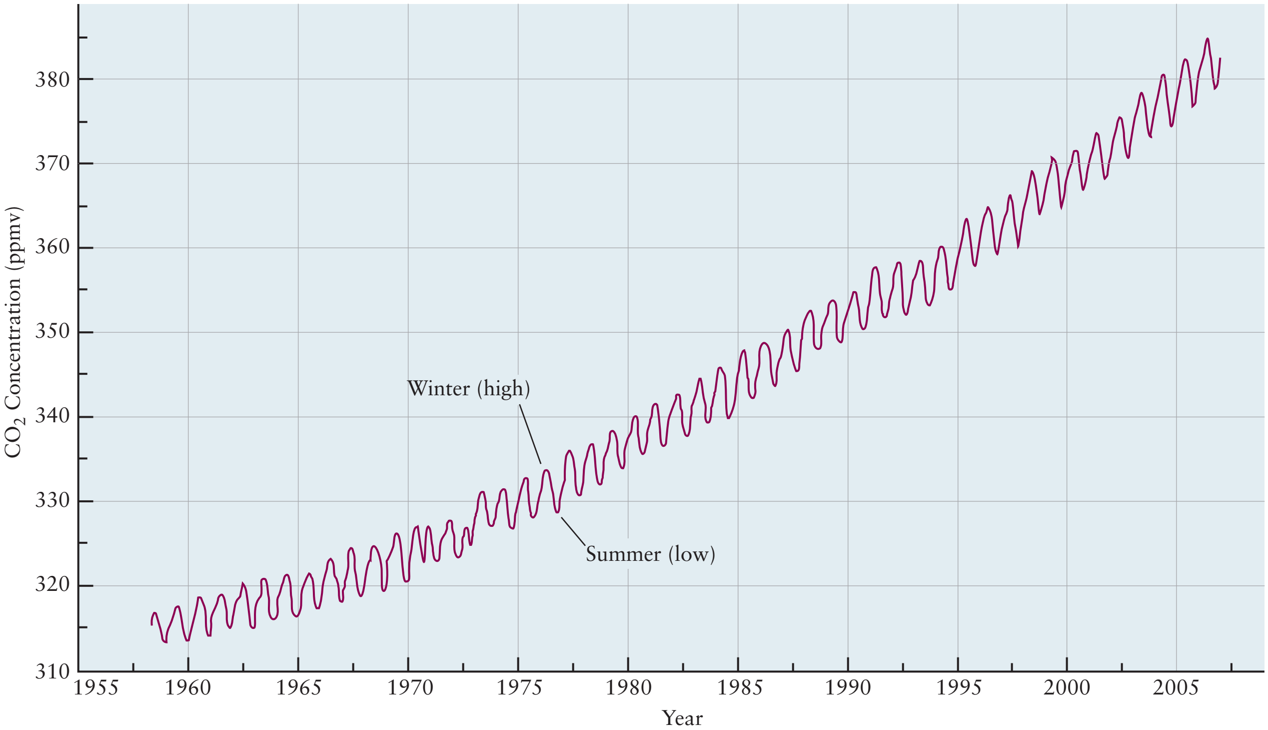


FIGURE 20.33 Worrisome trend: average monthly concentration of atmospheric CO$_2$ at Mauna Loa, Hawaii, 1958–2007. The concentration varies seasonally, caused by changes in carbon dioxide absorption by plants. (Data from www.cmdl.noaa.gov/ccgg/trends/co2_data_ml0.php, accessed on January 20, 2007.)

20.6 Photosynthesis

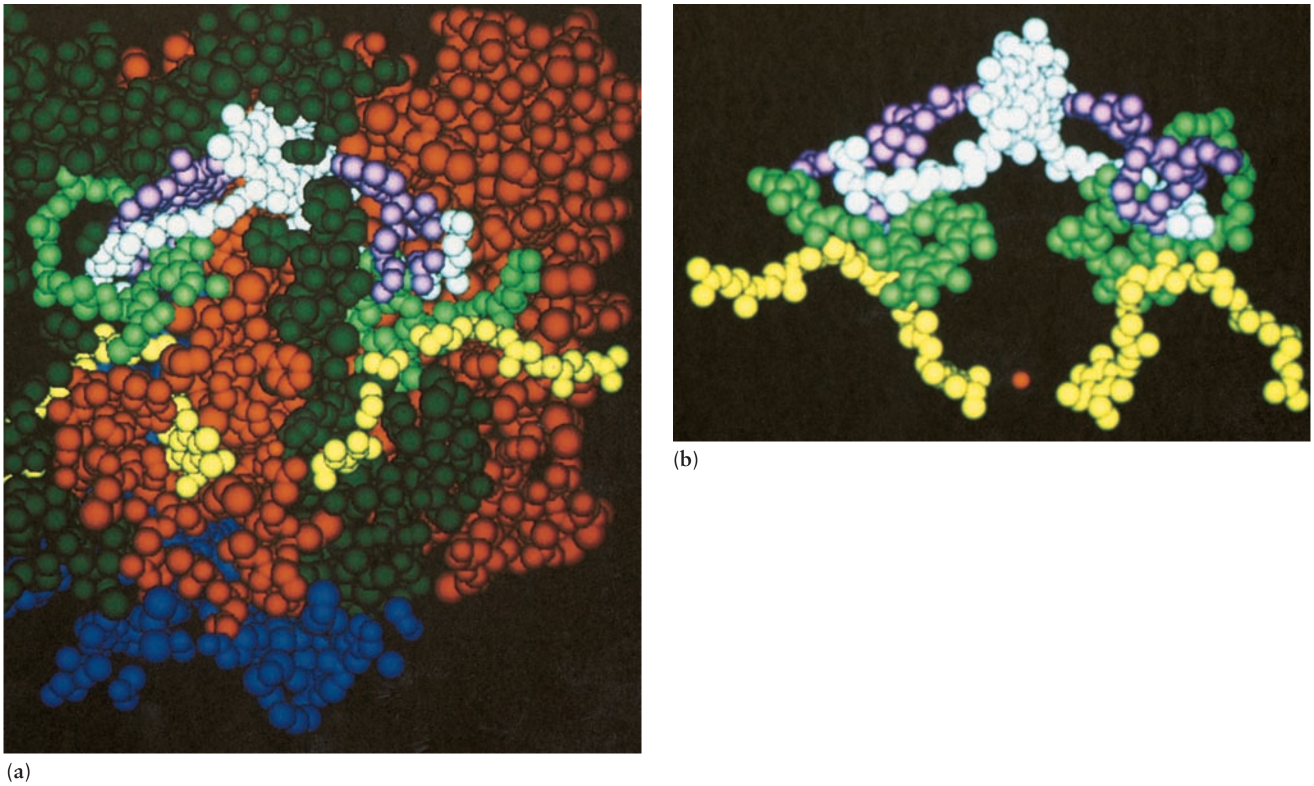
Even the most efficient manufactured solar collectors (see Section 22.8) fall far short of nature in their ability to convert solar energy from the sun into other useful forms of energy. Living species harvest light and store its energy by carrying out chemical reactions with positive free energy changes. For this purpose they use compounds dominated by carbon, in which metal ions play a critical role. This process of **photosynthesis** has transformed our planet and permitted the evolution of human life. Before we consider green plants (which provide most of the photosynthetic energy storage today), let us examine the reaction mechanisms in existent photosynthetic bacteria that are thought to have evolved earlier, and are considerably simpler, than plants. These bacteria have recently yielded some important secrets in experimental investigations.

The purple photosynthetic bacteria include the species *Rhodobacter sphaeroides* and *Rhodopseudomonas viridis*. Although these two differ in the details of their chemical makeup, the broad features of their mechanisms appear to be closely related. Their purple color reflects their absorption of light predominantly in the red region of the spectrum, with wavelengths up to 925 nm. *R. sphaeroides* and *R. viridis* use a variety of pigment molecules, including derivatives of chlorophyll (Fig. 8.22b), as "antennas" to absorb photons that reach their surface. The antenna molecules store the light energy through promotion of electrons to excited singlet states (see Fig. 20.11), then transfer this energy rapidly to other molecules nearby. In such a transfer the initially excited molecule returns to its ground state while a neighboring molecule reaches an excited singlet state. Within about 10^{-10} s (100 picoseconds), the energy migrates to the **reaction center** where it is trapped and is ready to be used in chemical reactions.

The initial trapping site in the reaction center consists of a **special pair** of bacteriochlorophyll molecules. The existence of this special pair was postulated in the

1960s by scientists who used magnetic resonance and absorption spectroscopy to probe the dynamics of the reaction center. Dramatic confirmation came in 1984 when three German chemists (Hartmut Michel, Johann Deisenhofer, and Robert Huber) prepared crystals of the membrane-bound reaction-center protein in *R. viridis* and determined its chemical structure by x-ray diffraction (see Section 21.1). Not only did they locate the bacteriochlorophyll molecules that form the special pair, but they also identified the positions of the molecules involved in the subsequent steps in photosynthesis.

Figure 20.34 shows the reaction center of the related bacterium *R. sphaeroides;* its structure is much more evident when the surrounding protein is stripped away. This complex consists of four bacteriochlorophyll molecules (the special pair and two others), two bacteriopheophytin molecules (which are bacteriochlorophyll molecules in which the central Mg ion is replaced by two hydrogen ions), two ubiquinone molecules (Fig. 20.35), and an iron(II) ion. Interestingly, these


(a)

(b)

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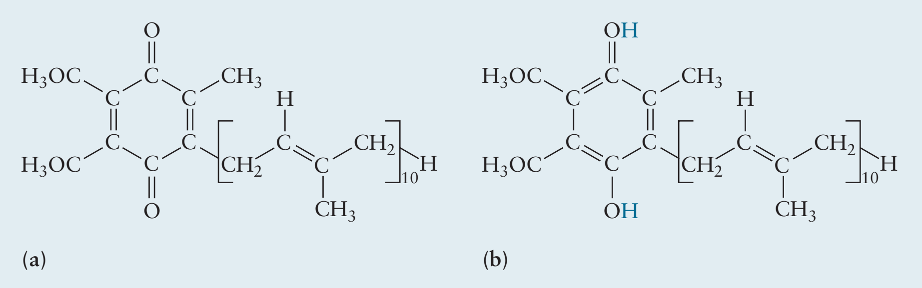
FIGURE 20.34 Computer-generated diagrams of the reaction center of the purple bacterium *R. sphaeroides* based on x-ray diffraction data. (a) The reaction center has been sliced through the middle to show the donor-acceptor molecules surrounded by protein (dark green, red, and blue portions). (b) The protein has been removed entirely. The four bacteriochlorophyll molecules are shown in white (for the special pair) and purple (for the other two); bacteriopheophytin molecules are light green; ubiquinone molecules are yellow. An iron(II) ion is shown between the ubiquinone molecules. The A branch is on the right, and the B branch is on the left.

FIGURE 20.35 The structures of (a) ubiquinone (UQ) and (b) its reduced form, UQH_2. Note the tail that contains a C_5H_8 group repeated ten times.



molecules are arranged in an almost perfectly symmetric fashion, with two branches (called A and B). But, the surrounding protein breaks the symmetry of the branches and causes the energy flow to pass almost entirely through the A branch (on the right in Fig. 20.34). Any energy passing through the B branch is too little to detect.

Time-resolved spectroscopy (see Fig. 20.21) has shown that within about 2.8 picoseconds (2.8×10^{-12} s) an electron is transferred from the special pair to the bacteriopheophytin molecule in the A branch, creating an anion on that site and leaving a cation on the special pair. Within 200 picoseconds, the electron reaches the ubiquinone molecule in the A branch and then is transferred across to the other ubiquinone molecule, in the B branch. The special pair picks up an electron from the iron atom in the heme group (see Fig. 8.22c) on a cytochrome protein outside the membrane and is reduced back to its original state. It then absorbs a second photon and transfers a second electron to the same B-branch ubiquinone molecule. This doubly reduced ubiquinone is less tightly bound to the reaction-center protein and moves away, being replaced by an unreduced ubiquinone molecule. The reduced ubiquinone gives up its electrons and hydrogen ions to another protein, which releases H^+ ions outside the cell membrane. The resulting hydrogen ion (proton) gradient across the cell wall stores energy (Recall from the Nernst equation in Chapter 17 that a voltage difference will exist across a concentration gradient.) and can carry out chemical reactions needed by the cell, ultimately transferring hydrogen ions back into the cell to close the cycle.

The chemical reactions at the reaction center can be summarized by the following six steps:

1. $(\mathrm{BChl})_2 + \mathrm{UQ} \xrightarrow[\text{light}]{} (\mathrm{BChl})_2^+ + \mathrm{UQ}^-$
2. $(\mathrm{BChl})_2^+ + \mathrm{Cyt} \longrightarrow (\mathrm{BChl})_2 + \mathrm{Cyt}^+$
3. $(\mathrm{BChl})_2 + \mathrm{UQ}^- \xrightarrow[\text{light}]{} (\mathrm{BChl})_2^+ + \mathrm{UQ}^{2-}$
4. $(\mathrm{BChl})_2^+ + \mathrm{Cyt} \longrightarrow (\mathrm{BChl})_2 + \mathrm{Cyt}^+$
5. $\mathrm{UQ}^{2-} + 2\,\mathrm{H}_{\mathrm{in}}^+ \longrightarrow \mathrm{UQH}_2$
6. $\underline{\mathrm{UQH}_2 + 2\,\mathrm{H}_{\mathrm{in}}^+ + 2\,\mathrm{Cyt}^+ \longrightarrow \mathrm{UQ} + 4\,\mathrm{H}_{\mathrm{out}}^+ + 2\,\mathrm{Cyt}}$

Overall: $4\,\mathrm{H}_{\mathrm{in}}^+ \longrightarrow 4\,\mathrm{H}_{\mathrm{out}}^+$

Here $(\mathrm{BChl})_2$ stands for the special pair of bacteriochlorophyll molecules, UQ for ubiquinone, and Cyt for the cytochrome protein. Steps 1 and 3 involve excitation of bacteriochlorophyll and transfer of a pair of electrons to a ubiquinone molecule. Steps 2 and 4 restore the special pair to its initial state. Steps 5 and 6 transfer hydrogen ions outside the membrane wall and restore the cytochrome to its reduced form. The net reaction is the light-driven movement of hydrogen ions from inside the cell to outside the cell.

Purple bacteria have only a single type of reaction center, but green plants have two types, referred to as photosystem I (PS I) and photosystem II (PS II). These absorb light at somewhat different wavelengths, allowing plants to use light energy from the sun more efficiently than purple bacteria do. Moreover, the two photosystems are linked to one another, so the excitation of PS II is followed by the excitation of PS I with a photon of longer wavelength. The cumulative effect of the two photons absorbed in series is the storage of a larger amount of energy than is available to purple bacteria. Whereas the bacteria use H_2S and other reduced compounds as sources of hydrogen, green plants are able to split abundant water molecules. In the process they give off oxygen, which is vital to the existence and survival of animal species on the planet.

Chemists are studying the structure and kinetics of the photosynthetic reaction center both to understand the fundamentals of this important natural process and to design new materials that mimic nature's ability to harvest light energy at such high efficiency. Artificial photosynthesis may lead to carbon-based materials that will replace the silicon collectors in solar cells in the 21st century. This will help reduce human dependence on stored fossil fuels as energy sources in the future.

CHAPTER SUMMARY

Spectroscopy—the study of the interaction between matter and radiation—has provided us with most of the data on which our understanding of the nature of molecules and reactions has been built. Each of the different kinds of motions of a molecule is quantized, and each one can be selectively excited by the absorption of electromagnetic radiation of the appropriate frequency. The energies of the motions increase in the order: nuclear spin flips, molecular rotations, molecular vibrations, electronic excitations. They are excited by radiofrequency, microwave, infrared, and visible and ultraviolet radiation, respectively. We obtain bond lengths and angles, bond strengths, and the energies of molecular orbitals from the spectra of molecules. Molecular spectroscopy is increasingly used in time-resolved and imaging modes, allowing us to follow molecular dynamics on time scales as short as 10^{-14} seconds and on length scales as short as 100 nm. Atmospheric chemistry is a vibrant science that is attacking problems of truly global scope—ozone destruction, air pollution, and global warming. Understanding the fundamentals of molecular spectroscopy and photochemistry is vital for us to make progress in solving these important problems.

CUMULATIVE EXERCISE

Bromine

Elemental bromine is a brownish red liquid that was first isolated in 1826. It is currently produced by oxidation of bromide ion in natural brines with elemental chlorine.

(a) What is the ground-state configuration of the valence electrons of bromine molecules (Br_2)? Is bromine paramagnetic or diamagnetic?

(b) What is the electron configuration of the Br_2^+ molecular ion? Is its bond stronger or weaker than that in Br_2? What is its bond order?

(c) Bromine compounds have been known and used for centuries. The deep purple color that symbolized imperial power in ancient Rome originated with the compound dibromoindigo, which was extracted in tiny quantities from purple snails (about 8000 snails per gram of compound). What color and maximum wavelength of *absorbed* light would give a deep purple (violet) color?

(d) What excited electronic state is responsible for the brownish red color of bromine? Refer to Figures 6.16 and 20.11.

(e) The two naturally occurring isotopes of bromine are ^{79}Br and ^{81}Br, with masses of 78.918 and 80.916 u, respectively. The wavelength of the $J = 0$ to $J = 1$ rotational transition in $^{79}Br^{81}Br$ is measured to be 6.18 cm. Use this information to calculate the bond length in the Br_2 molecule, and compare the result with that listed in Table 3.3.

(f) The wavelength of the vibrational transition in the $^{79}Br^{81}Br$ molecule is 3.09×10^{-5} m. Calculate the force constant for the bond in this molecule.

(g) The action of light on bromine compounds released into the air (such as by leaded gasoline) causes the formation of the BrO radical. Give the bond order of this species by comparing it with the related radical OF.

(h) There is concern that synthetic bromine-containing compounds, in addition to chlorofluorocarbons, are helping to destroy ozone in the stratosphere. The BrO [see part (g)] can take part with ClO in the following catalytic cycle:

$$Cl + O_3 \longrightarrow ClO + O_2$$

$$Br + O_3 \longrightarrow BrO + O_2$$

$$ClO + BrO \longrightarrow Cl + Br + O_2$$

Write the overall equation for this cycle.

Answers

(a) $(\sigma_{g4s})^2(\sigma^*_{u4s})^2(\sigma_{g4p_z})^2(\pi_{u4p})^4(\pi^*_{g4p})^4$; diamagnetic

(b) $(\sigma_{g4s})^2(\sigma^*_{u4s})^2(\sigma_{g4p_z})^2(\pi_{u4p})^4(\pi^*_{g4p})^3$; stronger; bond order is $\frac{3}{2}$ versus 1

(c) Yellow light, near 530 nm (see Figures 20.12 and 4.3).

(d) The lowest energy excited state, which arises from the excitation of an electron from the filled π^*_{g4p} orbital to the unfilled σ^*_{u4pz} orbital

(e) 2.28 Å (from Table 3.3: 2.286 Å)

(f) 247 J Nm^{-1}

(g) $\frac{3}{2}$ order

(h) Overall: $2\ O_3 \longrightarrow 3\ O_2$

CHAPTER REVIEW

Regions of the Electromagnetic Spectrum and Associated Molecular Transitions

- Radiofrequency—nuclear spin states, NMR spectroscopy
- Microwave—molecular rotations, bond lengths and bond angles
- Infrared—molecular vibrations, force constants
- Visible, ultraviolet—valence electron excitations

Experimental Methods in Molecular Spectroscopy

- A spectrophotometer measures the sample transmittance, $T = I_S/I_R$, which is the ratio of the light transmitted through the sample and that transmitted through a reference.
- The absorbance, $A = -\ln T$, measures the strength of the interaction between the molecule and the radiation.
- For most samples the absorption strength is proportional to the concentration, as expressed by the Beer–Lambert law: $A = \epsilon c \ell$, where A is the absorbance (dimensionless), ϵ is the molar extinction coefficient (L mol^{-1} cm^{-1}), c is the concentration in mols L^{-1}, and ℓ is the path length in cm.

Thermal Population of Molecular Energy Levels According to the Boltzmann Distribution

- Nuclear spin states are equally populated.
- Many excited rotational states are populated.
- Only the ground vibrational and electronic states are significantly populated at room temperature.

Rotational Spectroscopy

- Energy levels are given by

$$E_{\text{rot},\,J} = \frac{h^2}{8\pi^2 I}J(J+1) = hBJ(J+1) \qquad J = 0, 1, 2, \ldots$$

- Spectra consist of a series of lines equally spaced by $2B$, the rotational constant, which depends on the molecule's moment of inertia $I = \mu R_e^2$.
- Because many levels are populated at room temperature the intensities of the lines form an envelope, the shape of which can be used to measure temperature.
- Only molecules with permanent dipole moments absorb microwave radiation to excite rotations.

Vibrational Spectroscopy

- The harmonic oscillator model and the Morse potential are used to describe the vibrational motions of molecules.
- The dipole moment of the molecule must change during a vibration for that vibrational motion to be excited by the absorption of infrared radiation.

Excited Electronic States and Electronic Spectroscopy

- Electrons may be excited from occupied π molecular orbitals to unoccupied π^* molecular orbitals by absorbing visible or ultraviolet radiation.
- The particle-in-a-box model provides a good qualitative understanding of the orbital energies and absorption wavelengths of conjugated π systems, those that contain alternating single and double carbon-carbon bonds.

The Fate of Excited Electronic States

- Excited electronic states may return to the ground state of the same total spin by emitting radiation called fluorescence—it is generally intense and the excited state is very short-lived (nanoseconds).
- Excited electronic states may return to states with different total spin by emitting radiation called phosphorescence—it is generally very weak and the excited state lives for a rather long time (seconds).

Laser—Light Amplification by Stimulated Emission of Radiation

- The relative population of two electronic energy levels must be inverted from its equilibrium value to create an excess of excited states.
- Spontaneous emission initiates a chain reaction in which a series of stimulated emissions amplifies the number of photons enormously.

Time-resolved Spectroscopy

- Pulsed lasers with pulse durations as short as a few femtoseconds (10^{-15} s) provide detailed snapshots of fundamental physical and chemical processes such as the relaxation of excited electronic states and the formation and breaking of chemical bonds.

NMR Spectroscopy

- The energy of nuclear spin states is split in an externally applied magnetic field. The absorption of radiofrequency radiation can cause transitions between these two states.
- The chemical shift is a measure of the chemical environment of the proton.
- Spin-spin splitting identifies the number of equivalent protons attached to a carbon atom and is useful in identifying functional groups.

Stratospheric Chemistry

- Ozone is formed and destroyed in a series of stratospheric reactions. Its steady state concentration is described by the Chapman cycle.
- A class of refrigerants and propellants called chlorofluorocarbons (CFCs) produce chlorine radicals that catalytically destroy ozone.
- The ozone hole over Antarctica results from the storage of chlorine-containing molecules on the surfaces of polar stratospheric clouds during the Antarctic winter followed by sudden photolysis and release in the spring.

Tropospheric Chemistry

- Oxides of nitrogen (NO_x) and sulfur (SO_x), produced by the combustion of fossil fuels in vehicles and power plants are pollutants and also precursors to acid rain.

The Greenhouse Effect

- Energy provided by ultraviolet and visible radiation from the sun warms the Earth, which re-radiates in the infrared region of the electromagnetic spectrum.
- CO_2 absorbs infrared radiation very efficiently, causing the planet to be much warmer that if there were no CO_2 in the atmosphere.
- Atmospheric CO_2 concentrations and global temperatures are strongly correlated, as established by ice core data.
- The rise in CO_2 concentrations since the Industrial Revolution is thought to be largely due to human activities, and there is considerable concern over the possibility of significant warming in the coming decades.

CONCEPTS & SKILLS

After studying this chapter and working the problems that follow, you should be able to:

1. Apply the Beer–Lambert law to absorption spectra (Section 20.1, Problems 1–4).
2. Discuss the Boltzmann distribution of population among possible molecular quantum states (Sections 20.1 and 20.2, Problems 9, 10, 15, 16).
3. Relate the moments of inertia, bond lengths, and vibrational force constants of diatomic molecules to their rotational and vibrational spectra (Section 20.2, Problems 5–8, 11–14).
4. Describe the preparation of excited electronic states by absorption of radiation and the subsequent flow of energy (Section 20.3, Problems 17–24).
5. Describe the operation of laser devices (Section 20.3).
6. Discuss several new techniques in molecular spectroscopy and the purposes they serve (Section 20.3).
7. Outline the principles of magnetic resonance spectroscopy (Section 20.4, Problems 25–26).
8. Indicate processes in the atmosphere that are beneficial and those that are potentially damaging to the ecosystem (Section 20.5, Problems 27–30).
9. Explain the mechanism by which photosynthetic bacteria and green plants convert light energy to chemical energy. (Section 20.6, Problems 31–32).

KEY EQUATIONS

$$-\ln \frac{I_S}{I_R} = c\epsilon\ell = A \qquad \textbf{(Section 20.1)}$$

$$P(E_\mathrm{i}) = \mathrm{N}(E_\mathrm{i})/N_0 \propto \mathrm{g}(E_\mathrm{i}) \exp\left(-E_\mathrm{i}/k_\mathrm{B}T\right) \qquad \textbf{(Section 20.1)}$$

$$P(E_\mathrm{i})/P(E_\mathrm{f}) = g(E_\mathrm{i})/g(E_\mathrm{f}) \exp\left[-(E_i - E_f)/k_\mathrm{B}T\right] \qquad \textbf{(Section 20.1)}$$

$$I = \mu R_\mathrm{e}^2 \qquad \textbf{(Section 20.2)}$$

$$E_{\mathrm{rot},\,J} = \frac{h^2}{8\pi^2 I} J(J+1) = hBJ(J+1) \qquad J = 0, 1, 2, \ldots \qquad \textbf{(Section 20.2)}$$

$$\begin{aligned}
\nu = \frac{\Delta E}{h} &= \frac{h}{8\pi^2 I}\left[J_f(J_f+1) - J_\mathrm{i}(J_\mathrm{i}+1)\right] \\
&= \frac{h}{8\pi^2 I}\left[(J_\mathrm{i}+1)(J_\mathrm{i}+2) - J_\mathrm{i}(J_\mathrm{i}+1)\right] \\
&= \frac{h}{4\pi^2 I}(J_\mathrm{i}+1) = 2B(J_\mathrm{i}+1) \qquad J_\mathrm{i} = 0, 1, 2, \ldots \qquad \textbf{(Section 20.2)}
\end{aligned}$$

$$E_{\mathrm{vib},n} = h\nu\left(n + \tfrac{1}{2}\right) \qquad n = 0, 1, 2, \ldots \qquad \textbf{(Section 20.2)}$$

$$\delta = \frac{H_\mathrm{s} - H_\mathrm{r}}{H_\mathrm{r}} \times 10^6 \qquad \textbf{(Section 20.4)}$$

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G. Problems that are more challenging are indicated with asterisks.

General Aspects of Molecular Spectroscopy

1. The percentage transmittance of light at 250 nm through a certain aqueous solution is 20.0% at 25°C. The experimental cell length is 1.0 cm, and the concentration of the solution is 5×10^{-4} mol L^{-1}. Calculate the absorbance. Calculate the molar absorption coefficient.

2. Beer's law is used to measure the concentration of species in solutions, once a "standardization curve" has been prepared for that species. In one such experiment, percent transmission was measured for a series of solutions with known concentrations and the results were as follows:

Concentration μg mL^{-1}	1.0	2.0	3.0	4.0	5.0
Transmission, percent	66.8	44.7	29.2	19.9	13.3

Plot these results to obtain the standardization curve. An unknown concentration of the same species, measured in the same transmission cell, transmitted 35% of the incoming light. Calculate the concentration of the unknown solution.

3. Beer's law can be used to determine the concentration of two substances *A* and *B* in solution, provided they do not react or interact, so they absorb radiation independently. The following data were obtained for *A* and *B* in three different solutions:

	[A] mol L^{-1}	[B] mol L^{-1}	% Transmittance at λ = 400 nm	% Transmittance at λ = 500 nm
Solution 1	0.0010	0	10.0	60.0
Solution 2	0	0.0050	80.0	20.0
Solution 3	?	?	40.0	50.0

Calculate the concentrations of A and B in Solution 3.

4. The absorption of ultraviolet light by proteins at wavelength 280 nm is caused mostly by the amino acids tyrosine and tryptophan along the protein molecular chains. The molecular absorption coefficients for these two amino acids are:

$$\epsilon_{tryp}^{280} = 5690 \text{ L cm}^{-1} \text{ mol}^{-1}$$

$$^{280}_{tyro} = 1280 \text{ L cm}^{-1} \text{ mol}^{-1}$$

Experiments are carried out on a protein with molecular weight 26,000, which contains two units of tryptophan and six units of tyrosine along the chain. The absorption is measured in a cell 1 cm long, and the protein concentration is 1.0 mg mL^{-1}. Calculate the absorbance and the percent transmission.

Vibrations and Rotations of Molecules: Infrared and Microwave Spectroscopy

5. Use data from Tables 19.1 and 3.3 to predict the energy spacing between the ground state and the first excited rotational state of the $^{14}N^{16}O$ molecule.

6. Use data from Tables 19.1 and 3.3 to predict the energy spacing between the ground state and the first excited rotational state of the $^{1}H^{19}F$ molecule.

7. The first three absorption lines in the pure rotational spectrum of gaseous $^{12}C^{16}O$ are found to have the frequencies 1.15×10^{11}, 2.30×10^{11}, and 3.46×10^{11} s^{-1}. Calculate:
   (a) The moment of inertia *I* of CO (in kg m^2)
   (b) The energies of the $J = 1$, $J = 2$, and $J = 3$ rotational levels of CO, measured from the $J = 0$ state (in joules)
   (c) The C—O bond length (in angstroms)

8. Four consecutive absorption lines in the pure rotational spectrum of gaseous $^{1}H^{35}Cl$ are found to have the frequencies 2.50×10^{12}, 3.12×10^{12}, 3.74×10^{12}, and 4.37×10^{12} s^{-1}. Calculate:
   (a) The moment of inertia *I* of HCl (in kg m^2)
   (b) The energies of the $J = 1$, $J = 2$, and $J = 3$ rotational levels of HCl, measured from the $J = 0$ state (in joules)
   (c) The H—Cl bond length (in angstroms)
   (d) The initial and final *J* states for the observed absorption lines

9. In Example 20.1, we determined that the moment of inertia of the NaH molecule is 5.70×10^{-47} kg m^2.
   (a) Calculate the relative population of the $J = 5$ level and the ground state at 25°C.
   (b) Calculate the relative population of the $J = 15$ level and the ground state at 25°C.
   (c) Calculate the relative population of the $J = 25$ level and the ground state at 25°C.

10. The linear molecule N_2O has been examined by rotational spectroscopy. The N—N bond length was found to be 1.126 Å, and the N—O bond length was found to be 1.191 Å. From these results, we can calculate the moment of inertia to be 66.8×10^{-47} kg m^2 as shown in Fig. 20.6.
   (a) Calculate the relative population of the $J = 5$ level and the ground state at 25°C.
   (b) Calculate the relative population of the $J = 15$ level and the ground state at 25°C.
   (c) Calculate the relative population of the $J = 25$ level and the ground state at 25°C.

11. The Li_2 molecule (^{7}Li isotope) shows a very weak infrared line in its vibrational spectrum at a wavelength of 2.85×10^{-5} m. Calculate the force constant for the Li_2 molecule.

12. The Na_2 molecule (^{23}Na isotope) shows a very weak infrared line in its vibrational spectrum at a wavelength of 6.28×10^{-5} m. Calculate the force constant for the Na_2 molecule, and compare your result with that of problem 11. Give a reason for any difference.

13. The "signature" infrared absorption that indicates the presence of a C—H stretching motion in a molecule occurs at wavelengths near 3.4×10^{-6} m. Use this information to estimate the force constant of the C—H stretch. Take the reduced mass in this motion to be approximately equal to the mass of the hydrogen atom (a good approximation when the H atom is attached to a heavy group).

14. Repeat the calculation of the preceding problem for the N—H stretch, where absorption occurs near 2.9×10^{-6} m. Which bond is stiffer: N—H or C—H?

15. Estimate the ratio of the number of molecules in the first excited vibrational state of the molecule N_2 to the number in the ground state, at a temperature of 450 K. The vibrational frequency of N_2 is $7.07 \times 10^{13}\ s^{-1}$.

16. The vibrational frequency of the ICl molecule is $1.15 \times 10^{13}\ s^{-1}$. For every million ($1.00 \times 10^6$) molecules in the ground vibrational state, how many will be in the first excited vibrational state at a temperature of 300 K?

Excited Electronic States: Electronic Spectroscopy of Molecules

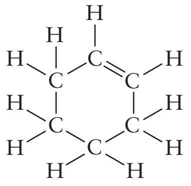
17. Suppose that an ethylene molecule gains an additional electron to give the $C_2H_4^-$ ion. Will the bond order of the carbon–carbon bond increase or decrease? Explain.

18. Suppose that an ethylene molecule is ionized by a photon to give the $C_2H_4^+$ ion. Will the bond order of the carbon–carbon bond increase or decrease? Explain.

19. The color of the dye "indanthrene brilliant orange" is evident from its name. In what wavelength range would you expect to find the maximum in the absorption spectrum of this molecule? Refer to the color spectrum in Figure 4.3.

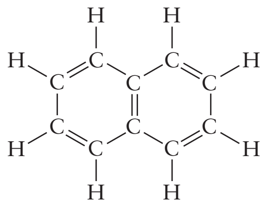
20. In what wavelength range would you expect to find the maximum in the absorption spectrum of the dye "crystal violet"?

21. The structure of the molecule cyclohexene is shown below:



Does the absorption of ultraviolet light by cyclohexene occur at shorter wavelengths than in benzene? Explain.

22. The naphthalene molecule has a structure that corresponds to two benzene molecules fused together:



The π-electrons in this molecule are delocalized over the entire molecule. The wavelength of maximum absorption in the UV-visible part of the spectrum in benzene is 255 nm. Is the corresponding wavelength shorter or longer than 255 nm for naphthalene?

23. Use data from Table 3.3 to give an upper bound on the wavelengths of light that are capable of dissociating a molecule of ClF.

24. Use data from Table 3.3 to give an upper bound on the wavelengths of light that are capable of dissociating a molecule of ICl.

Nuclear Magnetic Resonance Spectroscopy

25. Give the number of peaks and the relative peak areas that should be observed in the low-resolution proton magnetic resonance spectra of the following molecules:

$$CH_3CH_2CH_2CH_3,\ CH_3OCH_3,\ CH_3NHCH_3.$$

26. The organic compound 1,4-dimethylbenzene (also known as *p*-xylene) has the formula $(CH_3)_2C_6H_4$. Its structure has two CH_3 (methyl) groups substituted at opposite positions on the benzene (C_6H_6) ring. Predict the number of peaks in the low-resolution proton NMR spectrum of this compound and the relative areas of the peaks.

Introduction to Atmospheric Photochemistry

27. The bond dissociation energy of a typical C—F bond in a chlorofluorocarbon is approximately 440 kJ mol^{-1}. Calculate the maximum wavelength of light that can photodissociate a molecule of CCl_2F_2, breaking such a C—F bond.

28. The bond dissociation energy of a typical C—Cl bond in a chlorofluorocarbon is approximately 330 kJ mol^{-1}. Calculate the maximum wavelength of light that can photodissociate a molecule of CCl_2F_2, breaking such a C—Cl bond.

29. Draw a Lewis diagram(s) for the ozone molecule (O_3). Determine the steric number and hybridization of the central oxygen atom, and identify the molecular geometry. Describe the nature of the π bonds and give the bond order of the O—O bonds in ozone.

30. The compounds carbon dioxide (CO_2) and sulfur dioxide (SO_2) are formed by the burning of coal. Their apparently similar formulas mask underlying differences in molecular structure. Determine the shapes of these two types of molecules, identify the hybridization at the central atom of each, and compare the natures of their π bonds.

Photosynthesis

31. One way in which photosynthetic bacteria store chemical energy is through the conversion of a compound called adenosine diphosphate (ADP), together with hydrogen phosphate ion, to adenosine triphosphate (ATP):

$$ADP^{3-} + HPO_4^{2-} + H_3O^+ \longrightarrow ATP^{4-} + 2\ H_2O$$

$$\Delta G = +34.5\ \text{kJ (pH 7)}$$

Suppose some chlorophyll molecules absorb 1.00 mol of photons of blue light with wavelength 430 nm. If *all* this energy could be used to convert ADP to ATP at room conditions and pH 7, how many molecules of ATP would be produced per photon absorbed? (The actual number is smaller because the conversion is not 100% efficient.)

32. Repeat the calculation of the preceding problem for red light with wavelength 700 nm.

ADDITIONAL PROBLEMS

33. What are the moments of inertia of $^1H^{19}F$ and $^1H^{81}Br$, expressed in kg m^2? Compute the spacings $\nu = \Delta E/h$ of the rotational states, in s^{-1}, between $J = 0$ and 1 and between $J = 1$ and 2. Explain, in one sentence, why the large change in mass from 19 to 81 causes only a small change in rotational energy differences.

34. The average bond length of a molecule can change slightly with vibrational state. In $^{23}Na^{35}Cl$, the frequency of light absorbed in a change from the $J = 1$ to the $J = 2$ rotational state in the ground vibrational state ($n = 0$) was measured to be $\nu = 2.60511 \times 10^{10}\ s^{-1}$, and that for a change from $J = 1$ to $J = 2$ in the first excited vibrational state ($n = 1$) was $\nu = 2.58576 \times 10^{10}\ s^{-1}$. Calculate the average bond lengths of NaCl in these two vibrational states, taking the relative atomic mass of ^{23}Na to be 22.9898 and that of ^{35}Cl to be 34.9689.

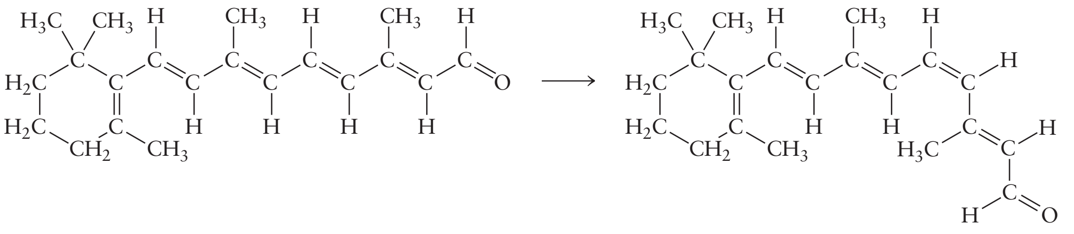
35. The vibrational frequencies of $^{23}Na^{1}H$, $^{23}Na^{35}Cl$, and $^{23}Na^{127}I$ are $3.51 \times 10^{13}\ s^{-1}$, $1.10 \times 10^{13}\ s^{-1}$, and $0.773 \times 10^{13}\ s^{-1}$, respectively. Their bond lengths are 1.89 Å, 2.36 Å, and 2.71 Å. What are their reduced masses? What are their force constants? If NaH and NaD have the same force constant, what is the vibrational frequency of NaD? D is ^{2}H.

36. Recall that nuclear spin states in nuclear magnetic resonance are typically separated by energies of 2×10^{-5} kJ mol^{-1} to 2×10^{-4} kJ mol^{-1}. What are the ratios of occupation probability between a pair of such levels at thermal equilibrium and a temperature of 25°C?

37. The vibrational temperature of a molecule prepared in a supersonic jet can be estimated from the observed populations of its vibrational levels, assuming a Boltzmann distribution. The vibrational frequency of HgBr is $5.58 \times 10^{12}\ s^{-1}$, and the ratio of the number of molecules in the $n = 1$ state to the number in the $n = 0$ state is 0.127. Estimate the vibrational temperature under these conditions.

38. An electron in the π orbital of ethylene (C_2H_4) is excited by a photon to the π^* orbital. Do you expect the equilibrium bond length in the excited ethylene molecule to be greater or less than that in ground-state ethylene? Will the vibrational frequency in the excited state be higher or lower than in the ground state? Explain your reasoning.

39. One isomer of retinal is converted to a second isomer by the absorption of a photon:



This process is a key step in the chemistry of vision. Although free retinal (in the form shown to the left of the arrow) has an absorption maximum at 376 nm, in the ultraviolet region of the spectrum this absorption shifts into the visible range when the retinal is bound in a protein, as it is in the eye.

(a) How many of the C=C bonds are *cis* and how many are *trans* in each of the preceding structures? (When assigning labels, consider the relative positions of the two largest groups attached at each double bond.) Describe the motion that takes place upon absorption of a photon.

(b) If the ring and the —CHO group in retinal were replaced by $-CH_3$ groups, would the absorption maximum in the molecule shift to longer or shorter wavelengths?

* **40.** The ground-state electron configuration of the H_2^+ molecular ion is $(\sigma_{g1s})^1$.

(a) A molecule of H_2^+ absorbs a photon and is excited to the σ_{u1s}^* molecular orbital. Predict what happens to the molecule.

(b) Another molecule of H_2^+ absorbs even more energy in an interaction with a photon and is excited to the σ_{g2s} molecular orbital. Predict what happens to this molecule.

* **41.** **(a)** Draw a Lewis diagram for formaldehyde (H_2CO), and decide the hybridization of the central carbon atom.

(b) Formulate the molecular orbitals for the molecule.

(c) A strong absorption is observed in the ultraviolet region of the spectrum and is attributed to a $\pi \longrightarrow \pi^*$ transition. Another, weaker transition is observed at lower frequencies. What electronic excitation causes the weaker transition?

42. Write balanced chemical equations that describe the formation of nitric acid and sulfuric acid in rain, starting with the sulfur in coal and the oxygen, nitrogen, and water vapor in the atmosphere.

43. Compare and contrast the roles of ozone (O_3) and nitrogen dioxide (NO_2) in the stratosphere and in the troposphere.

44. Describe the greenhouse effect and its mechanism of operation. Give three examples of energy sources that contribute to increased CO_2 in the atmosphere and three that do not.

45. Draw a schematic diagram of the steps in bacterial photosynthesis, numbering them in sequence and showing the approximate spatial relations of the involved molecules.

46. Do you expect the energy of the special pair of bacteriochlorophyll molecules to be higher or lower than the energy of an isolated bacteriochlorophyll? (*Hint:* Think about the analogy between the mixing of atomic orbitals to make molecular orbitals and the mixing of molecular orbitals on two nearby molecules.)

CUMULATIVE PROBLEMS

47. At thermal equilibrium, is the rate as a molecule is excited from $n = 0$ to the $n = 1$ level greater than or less than the rate for the reverse process? What is the ratio of the rate constants? (*Hint:* Think of the analogy with the chemical equilibrium between two species.)

* **48.** It is important to know the dissociation constant of an indicator in order to use it properly in acid–base titrations. Spectrophotometry can be used to measure the concentration of these intensely colored species in acidic versus basic solutions, and from these data the equilibrium between the acidic and basic forms can be calculated. In one such study on the indicator *m*-nitrophenol, a 6.36×10^{-4} M solution was examined by spectrophotometry at 390 nm and 25°C in the following experiments. In highly acidic solution, where essentially all the indicator was in the form HIn, the absorbance was 0.142. In highly basic solution, where essentially all of the indicator was in the form In^-, the absorbance was 0.943. In a further series of experiments, the pH was adjusted using a buffer solution of ionic strength I, and absorbance was measured at each pH value. The following results were obtained:

pH	I	A
8.321	0.10	0.527
8.302	0.08	0.518
8.280	0.06	0.505
8.251	0.04	0.493
8.207	0.02	0.470

Calculate pK_a for the indicator at each value of ionic strength.

49. The hydroxyl radical has been referred to as the "chief clean-up agent in the troposphere." Its concentration is approximately zero at night and becomes as high as 1×10^7 molecules per cm^3 in highly polluted air.

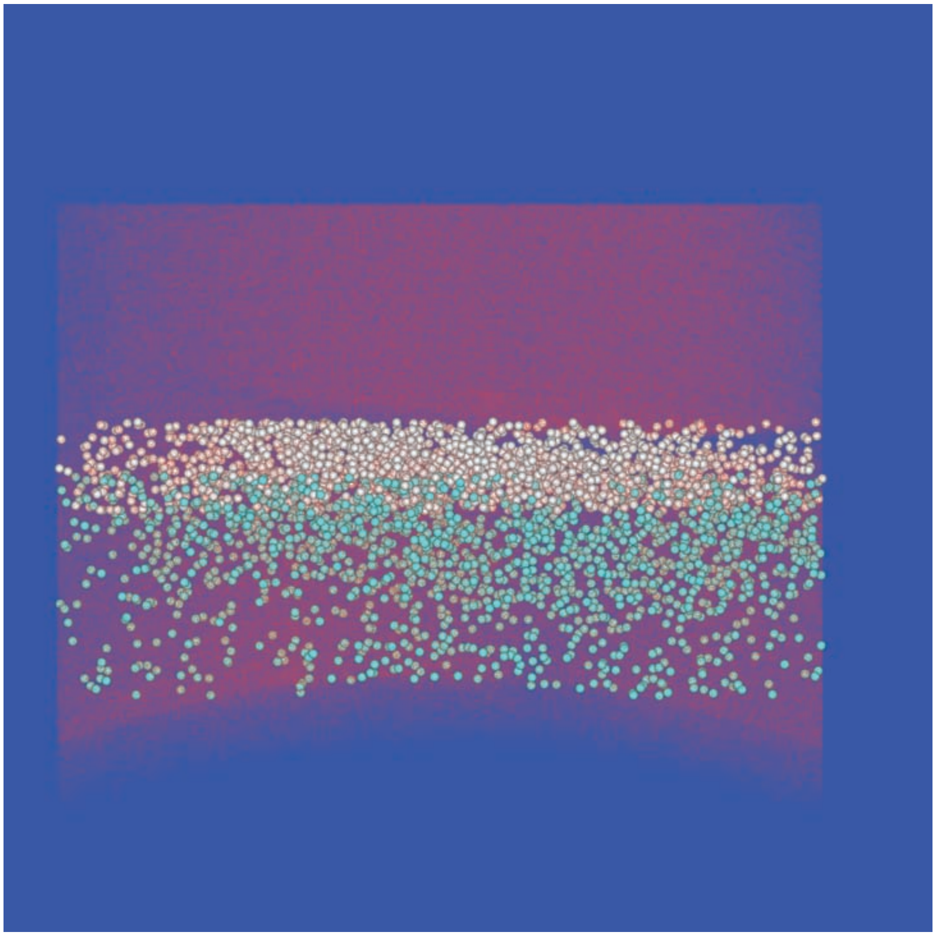
(a) Calculate the maximum mole fraction and partial pressure of OH in polluted air at 25°C and atmospheric pressure.

(b) Write an equation for the reaction of HO with NO_2 in the atmosphere. How does the oxidation state of nitrogen change in this reaction? What is the ultimate fate of the product of this reaction?

50. In unpolluted air at 300 K, the hydroxyl radical OH reacts with CO with a bimolecular rate constant of 1.6×10^{11} L mol^{-1} s^{-1} and with CH_4 with a rate constant of 3.8×10^9 L mol^{-1} s^{-1}. Take the partial pressure of CO in air to be constant at 1.0×10^{-7} atm and that of CH_4 to be 1.7×10^{-6} atm, and assume that these are the primary mechanisms by which OH is consumed in the atmosphere. Calculate the half-life of OH under these conditions.

UNIT VI

Materials



Courtesy of Imago Scientific Instruments Corporation

Cross-sectional view of a three-dimensional map of dopant atoms (light blue spheres) implanted into a typical silicon transistor structure. Red dots represent the silicon atoms (only 2% are shown for clarity) and the gray spheres represent a native silicon dioxide layer located at the interface between the crystalline silicon substrate and layer of deposited polycrystalline silicon.

Throughout history, the discovery of new materials from which to fashion the structures, machines, and devices of everyday life has set off great change in human affairs. Modern science and engineering—with chemistry in the central role—provide routes for modifying properties of materials to meet specific applications and for synthesizing and processing new materials designed from the beginning to have specific properties. The mechanical, thermal, electrical, and optical properties of a material depend on the extended nano-structural arrangement of chemical bonds within it. This arrangement can be created, modified, and tailored through chemical reactions. The contemporary disciplines of materials chemistry, solid state chemistry, and materials science and engineering—among the most active branches of chemistry today—all rely on the "properties↔structure↔reactions" correlation to make the leap from chemical bonding in isolated molecules (Unit II) to engineering applications.

UNIT CHAPTERS

CHAPTER 21
Structure and Bonding in Solids

CHAPTER 22
Inorganic Solid Materials

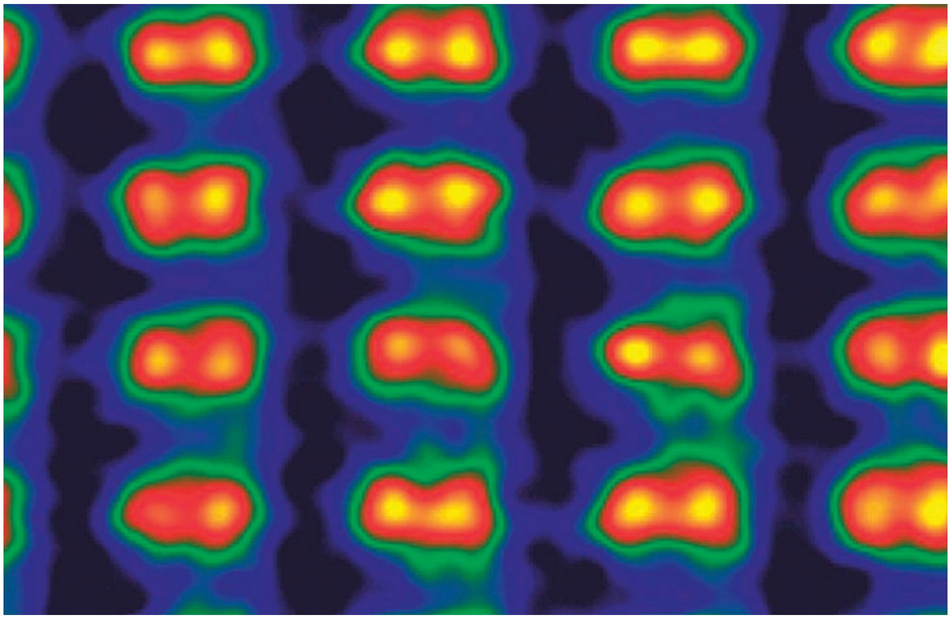
CHAPTER 23
Polymeric Materials and Soft Condensed Matter

UNIT GOALS

- To study the relationship between crystal symmetry and atomic-level structure as revealed by x-ray diffraction experiments
- To survey chemical bonding in classes of solids and correlate bonding with the properties of solids
- To explore three essential classes of materials—ceramics, optical and electronic materials, and polymers
- To illustrate the role of modern chemistry in measuring properties and identifying applications for both natural and manufactured materials

CHAPTER 21

Structure and Bonding in Solids



Courtesy of Oak Ridge National Laboratory

Pairs of silicon atoms separated by only 0.78 Å are clearly resolved in this ultrahigh-resolution electron microscope image.

In this chapter we begin a radical departure from the emphasis on the single molecule that permeates the previous twenty chapters. Unit II describes the chemical bonding and structure of single, isolated molecules. Unit III explains the macroscopic properties of gases and liquids through intermolecular forces that originate in the structures of individual molecules. While the behavior of many molecules contributes to these properties, the mechanism of their contribution is essentially that a few molecules come close enough to a "target" molecule to experience the intermolecular forces it sets up. Units IV and V deal with the equilibrium and rate aspects of chemical reactions as consequences of collisions between individual molecules.

The behavior of solids is a different story altogether. Chapter 10 identifies *rigidity* as the unique characteristic of solids, in dramatic contrast to the fluidity of gases and liquids. A rigid material retains its shape when an external mechanical force, called stress, is applied. A rigid material shows structural strength by not flowing under stress. All classes of solids behave this way because—with one exception—they are not collections of molecules held together by intermolecular forces. Rather, solids are extended arrays of strong chemical bonds between atoms, almost as if they were "super-molecules." These arrays extend over macroscopic distances, and it is the *collective behavior* of this set of chemical bonds that imparts strength and rigidity to solids.


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FIGURE 21.1 Microcrystals of realgar, As_4S_4.

Solids whose structures are highly ordered and symmetrical over macroscopic distances are called **crystals.** Although the symmetry and beauty of crystals have always excited curiosity and wonder, the science of **crystallography** began only in the latter part of the 18th century. In those closing days of the Age of Enlightenment—while Lavoisier led the modern approach to chemistry—another brilliant French thinker established the fundamental laws of crystallography. René-Just Haüy was struck by the observation that when he accidentally dropped a crystal of calcite (a form of calcium carbonate), it fractured into smaller crystals with the same interfacial angles between their planar surfaces as in the original crystal. The statement that constant interfacial angles are observed when crystals are cleaved is now known as **Haüy's law.** Haüy concluded that the outward symmetry of crystals (Fig. 21.1) implies a highly regular internal structure and the existence of a smallest crystal unit. His inferences were correct. What distinguishes the crystalline state from the gaseous and liquid states is the nearly perfect positional order of the atoms, ions, or molecules in crystals. This crystalline order has been confirmed experimentally by x-ray diffraction and explained theoretically by the quantum theory of solids.

We begin this chapter with a look at the microscopic structure of a perfect crystal, and establish the methods for determining structure and the language for describing it. We then examine the types of chemical bonding in solids, identifying the forces that hold together different kinds of solids. The perfect crystal is the idealized model for investigations in solid state science, just as the ideal gas is the starting point for studies of fluid behavior. We use it as the point of reference for describing less ordered condensed phases of matter—defective crystals and amorphous solids—in terms of their deviations from perfect order and the consequent changes in properties. We end the chapter with a brief introduction to diffusion in solids, the mechanism by which a free atom migrates through an extended solid state structure. Diffusion has great influence on the rate and equilibrium of chemical reactions in the solid state and on tailoring the properties of the solids through carefully controlled incorporation of impurities.

21.1 Crystal Symmetry and the Unit Cell

The unifying aspect of crystal structure is the repetition, over long distances, of the same basic structural features in the arrangement of the atoms. The most fundamental way to characterize and classify these structures is based on the numbers and kinds of their **symmetry elements.** When the result of rotation, reflection, or inversion of an object can be exactly superimposed on the original object—that is, matched point for point to the original object—the structure is said to contain the corresponding symmetry element. Examples include an axis of rotation, a plane of reflection (mirror plane), or a central point (inversion center), as shown in Figure 21.2. These symmetry operations can be applied to geometrical shapes, to physical objects, and to molecular structures.

Consider a cube as an example. Suppose the center of the cube is placed at the origin of its coordinate system and the symmetry operations that transform it into identity with itself are counted (Fig. 21.3). The x, y, and z coordinate axes are 4-fold axes of rotational symmetry, denoted by C_4, because a cube that is rotated through a multiple of 90° (= 360°/4) about any one of these axes is indistinguishable from the original cube. Similarly, a cube has four 3-fold axes of rotational

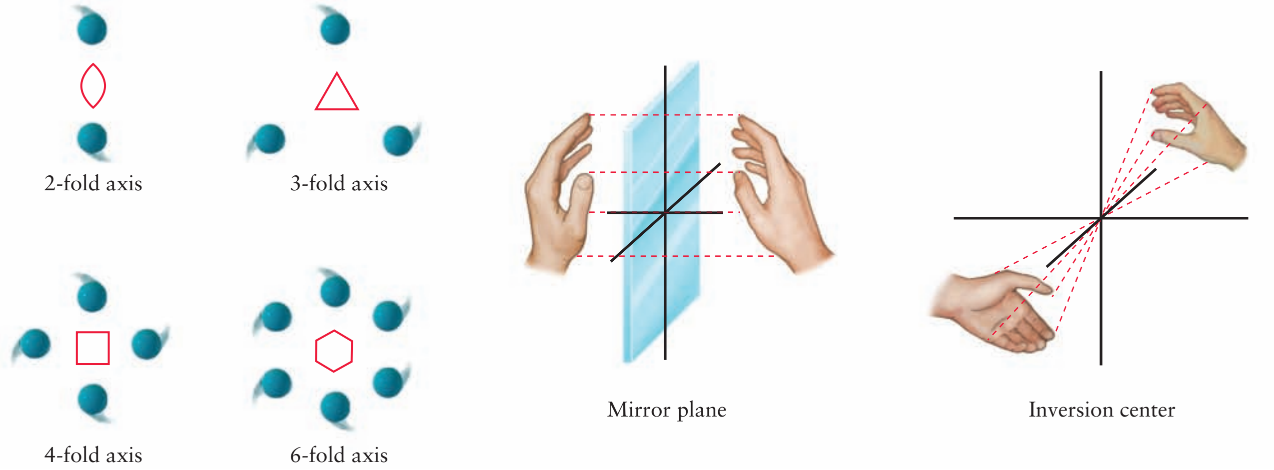


FIGURE 21.2 Three types of symmetry operation: rotation about an *n*-fold axis, reflection in a plane, and inversion through a point.

symmetry, designated C_3, that are the body diagonals of the cube, connecting opposite vertices. In addition, a cube has six 2-fold rotational axes of symmetry, defined by the six axes that pass through the centers of edges and through the coordinate origin. Next, the cube has nine mirror planes of symmetry (designated by the symbol m), which reflect any point in one half of the cube into an equivalent point in the other half. Finally, a cube has a center of inversion (reflection through a point, designated i).

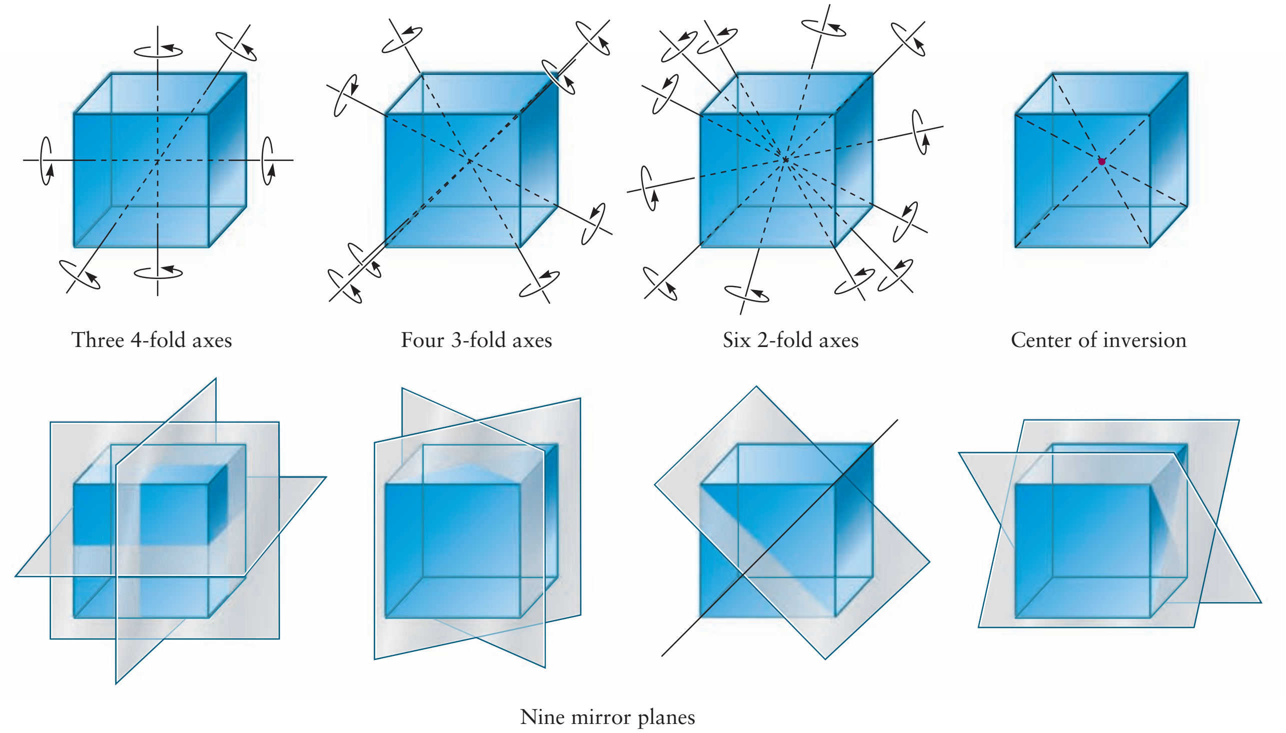


FIGURE 21.3 Symmetry operations acting on a cube. The various rotations of the cube are suggested by the curved arrows around the rotational axes.

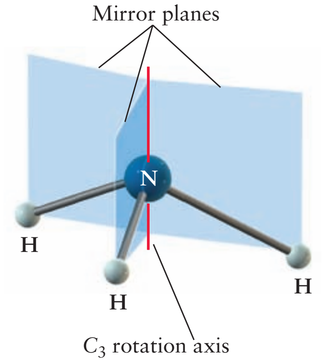


FIGURE 21.4 An ammonia molecule has a 3-fold axis of rotation and three mirror planes of symmetry. Each of the N—H bonds lies in a mirror plane.

EXAMPLE 21.1

Identify the symmetry elements of the ammonia molecule (NH_3).

SOLUTION

If the ammonia molecule is drawn as a pyramid with the nitrogen atom at the top (Fig. 21.4), then the only axis of rotational symmetry is a 3-fold axis passing downward through the N atom. Three mirror planes intersect at this 3-fold axis.

Related Problems: 3, 4

Unit Cells in Crystals

The symmetry operations just described can be applied to crystals as well as to individual molecules or shapes. Identical sites within a crystal recur regularly because of long-range order in the organization of the atoms. The three-dimensional array made up of all the points within a crystal that have the same environment in the same orientation is a **crystal lattice.** Such a lattice is an abstraction "lifted away" from a real crystal, embodying the scheme of repetition at work in that crystal. The lattice of highest possible symmetry is that of the **cubic system.** This lattice is obtained by filling space with a series of identical cubes, which are the **unit cells** in the system. A single unit cell contains all structural information about its crystal, because in principle the crystal could be constructed by making a great many copies of a single original unit cell and stacking them in a three-dimensional array. Unit cells fill space.

Other crystal systems besides cubic can be defined by their own unique unit cells. Constraints of symmetry permit only seven types of three-dimensional lattices. Each type has a unit cell with the shape of a parallelepiped (Fig. 21.5), whose size and shape are fully described by three edge lengths (a, b, and c) and the three angles between those edges (α, β, and γ). These lengths and angles are the **cell constants.** The symmetry that defines each of the seven crystal systems imposes conditions on the shape of the unit cell summarized in relations among the cell constants (Table 21.1, Fig. 21.6). The unit cell chosen is the smallest unit that has all the symmetry elements of the crystal lattice; there is no benefit in using large cells once all the symmetry elements have been included. A unit cell of the minimum size is **primitive** and shares each of the eight **lattice points** at its corners with seven other unit cells, giving one lattice point per unit cell.

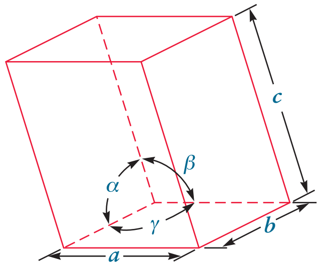


FIGURE 21.5 Unit cells always have three pairs of mutually parallel faces. Only six pieces of information are required to construct a scale model of a unit cell: the three cell edges (a, b, and c) and the three angles between the edges (α, β, and γ). By convention, γ is the angle between edges a and b, α the angle between b and c, and β the angle between a and c.

TABLE 21.1 The Seven Crystal Systems

Crystal System	Minimum Essential Symmetry	Conditions on Unit-Cell Edges and Angles
Hexagonal	One 6-fold rotation	$a = b$; $\alpha = \beta = 90°$, $\gamma = 120°$
Cubic	Four independent 3-fold rotations[†]	$a = b = c$; $\alpha = \beta = \gamma = 90°$
Tetragonal	One 4-fold rotation	$a = b$; $\alpha = \beta = \gamma = 90°$
Trigonal	One 3-fold rotation	$a = b = c$; $\alpha = \beta = \gamma \neq 90°$
Orthorhombic	Three mutually perpendicular 2-fold rotations	$\alpha = \beta = \gamma = 90°$
Monoclinic	One 2-fold rotation	$\alpha = \beta = 90°$
Triclinic	No symmetry required	None

[†] Each of these axes makes 70.53° angles with the other three.

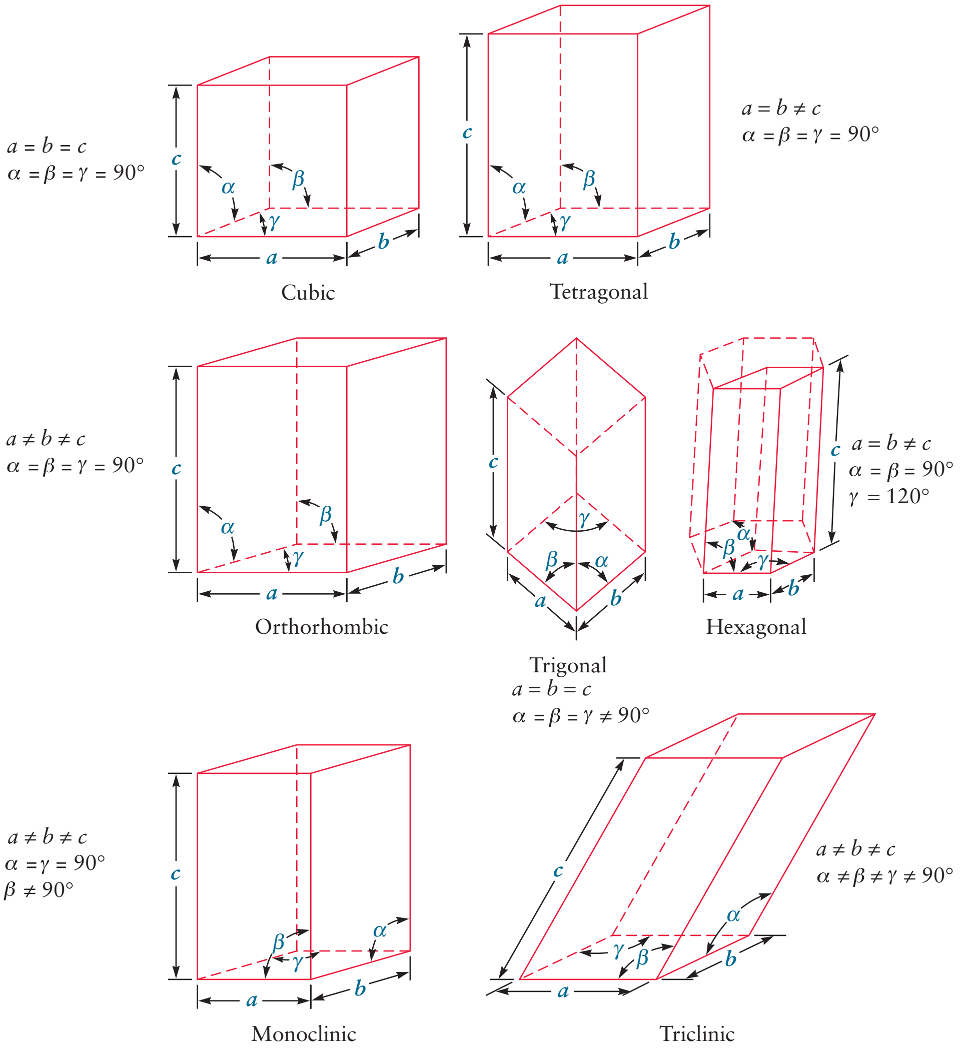


FIGURE 21.6 Shapes of the unit cells in the seven crystal systems. The more symmetric crystal systems have more symmetric cells.

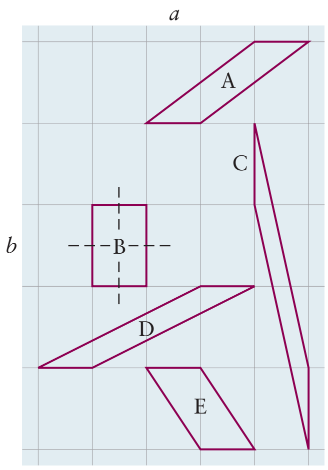


FIGURE 21.7 Cells with and without mirror planes in a two-dimensional lattice. Each cell has the same area, but only cell B possesses mirror planes in addition to the 2-fold rotation axes required by the lattice.

Other possible unit cells with the same volume (an infinite number, in fact) could be constructed, and each could generate the macroscopic crystal by repeated elementary translations, but only those shown in Figure 21.6 possess the symmetry elements of their crystal systems. Figure 21.7 illustrates a few of the infinite number of cells that can be constructed for a two-dimensional rectangular lattice. Only the rectangular cell B in the figure has three 2-fold rotation axes and two mirror planes. Although the other cells all have the same area, each of them has only one 2-fold axis and no mirror planes; they are therefore not acceptable unit cells.

Sometimes the smallest, or primitive, unit cell does not have the full symmetry of the crystal lattice. If so, a larger *nonprimitive* unit cell that does have the characteristic symmetry is deliberately chosen (Fig. 21.8). Only three types of nonprimitive cells are commonly used in the description of crystals: **body-centered, face-centered,** and **side-centered.** They are shown in Figure 21.9.

Scattering of X-Rays by Crystals

In the 19th century, crystallographers could classify crystals into the seven crystal systems only on the basis of their external symmetries. They could not measure the dimensions of unit cells or the positions of atoms within them. Several

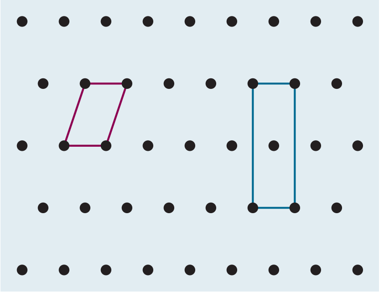


FIGURE 21.8 In this two-dimensional lattice, every lattice point is at the intersection of a horizontal mirror line and a vertical mirror line. It is possible to draw a primitive unit cell (red), but the larger, centered unit cell (blue) is preferred because it also has two mirror lines, the full symmetry of the lattice. A similar argument applies to the choice of unit cells on three-dimensional lattices.

developments by German physicists changed this situation at the turn of the century. Wilhelm Roentgen's discovery of x-rays in 1895 provided a tool of enormous power for determining the structures of crystals. Max von Laue suggested that crystals might serve as three-dimensional gratings for the diffraction of electromagnetic radiation with a wavelength comparable to the distance between planes of atoms. Friedrich and Knipping demonstrated experimentally in 1912 that this was indeed the case, and von Laue was awarded the Nobel Prize in physics in 1914 for his theory of the diffraction of x-rays by crystals. At about the same time, W. H. Bragg and W. L. Bragg (father and son) at Cambridge University in England also demonstrated the diffraction of x-rays by crystals and shared the Nobel Prize in physics the following year. (W. L. Bragg was 22 years old and still a student at Cambridge when he discovered the diffraction law.) The formulation of the diffraction law proposed by the Braggs is equivalent to von Laue's suggestion and somewhat simpler to visualize. So we will follow an approach similar to theirs.

When electromagnetic radiation passes through matter, it interacts with the electrons in atoms, and some of it is scattered as spherical waves going out from the atoms in the solid. Suppose that x-radiation strikes two neighboring scattering centers. The expanding spheres of scattered waves soon encounter each other and interfere. In some directions, the waves are in phase and reinforce each other, or interfere *constructively* (Fig. 21.10a); in others they are out of phase and cancel each other out, or interfere *destructively* (see Fig. 21.10b). Constructive interference occurs when the paths traversed by two waves differ in length by a whole number of wavelengths. The amplitudes of waves that interfere constructively add to one another, and the intensity of the scattered radiation in that direction is proportional to the square of the total amplitude.

Figure 21.11 illustrates the constructive interference of x-rays scattered by the electrons in atoms in equally spaced planes separated by the distance d. A parallel bundle of coherent x-rays of a single known wavelength is allowed to fall on the surface of a crystal, making an angle θ with a set of parallel planes of atoms in the crystal. The scattering angle 2θ is then varied by rotating the crystal about an axis perpendicular to the plane of the figure. Line AD in Figure 21.11 represents a wave front of waves that are in phase as they approach the crystal. The wave that is

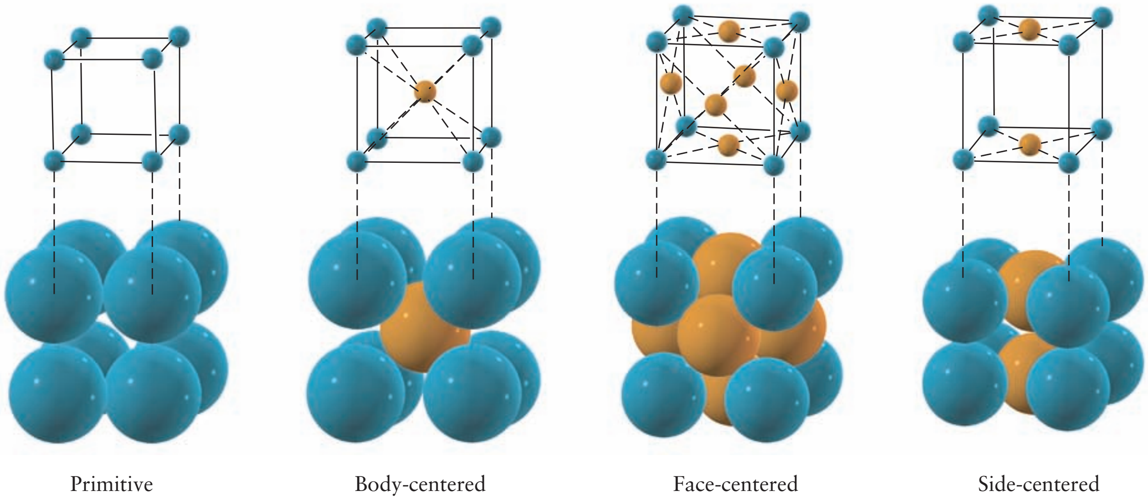
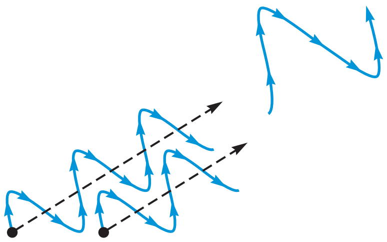
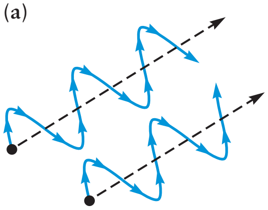


FIGURE 21.9 Centered lattices, like all lattices, have lattice points at the eight corners of the unit cell. A body-centered lattice has an additional lattice point at the center of the cell, a face-centered lattice has additional points at the centers of the six faces, and a side-centered lattice has points at the centers of two parallel sides of the unit cell. (**Note:** The colored dots in the lattice diagrams represent lattice points, not atoms.)



Scattering centers
(a)



Scattering centers
(b)

FIGURE 21.10 A beam of x-rays (not shown) is striking two scattering centers, which emit scattered radiation. The difference in the lengths of the paths followed by the scattered waves determines whether they interfere (a) constructively or (b) destructively. This path difference depends on both the distance between the centers and the direction in which the scattered waves are moving.

scattered at B follows the path ABC, and the one that is scattered at F follows the path DFH. The second wave travels a greater distance than the first, and the difference in path length is the sum of the two segments EF and FG. To achieve constructive interference in the scattered waves (that is, for the phases to be the same along the wave front CH), this additional distance traveled by the second wave must be an integral multiple of the x-ray wavelength λ:

$$\mathrm{EF} + \mathrm{FG} = n\lambda \qquad n = 1, 2, 3, \ldots$$

From trigonometry, the lengths of these two segments are equal to each other and to $d \sin \theta$, where d is the interplanar spacing. Therefore, constructive interference occurs only when

$$n\lambda = 2d \sin \theta \qquad n = 1, 2, 3, \ldots \tag{21.1}$$

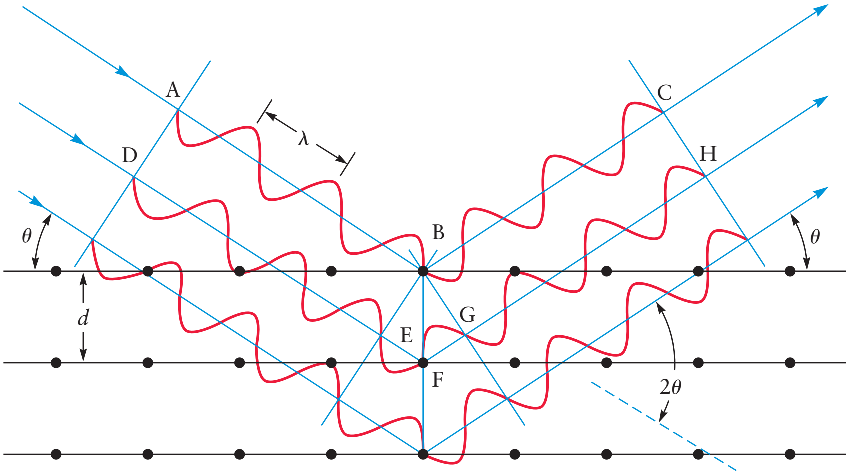
It is easy to verify that for angles that meet this condition, the waves scattered from the third and subsequent planes are also in phase with the waves scattered from the first two planes.

The preceding condition on allowed wavelengths is called the **Bragg law,** and the corresponding angles are called **Bragg angles** for that particular set of parallel planes of atoms. It appears as though the beam of x-rays has been reflected symmetrically from those crystal planes, and we often speak colloquially of the "Bragg reflection" of x-rays. The x-rays have not been reflected, however, but have undergone constructive interference, more commonly called diffraction. The case $n = 1$ is called first-order Bragg diffraction, $n = 2$ is second-order, and so forth.

We now possess a tool of immense value for determining the interplanar spacings of crystals. If a crystal is turned through different directions, other parallel sets of planes with different separations are brought into the Bragg condition. The symmetry of the resulting diffraction pattern identifies the crystal system, and the Bragg angles determine the cell constants. Moreover, the *intensities* of the diffracted beams permit the locations of the atoms in the unit cell to be determined.

Analogous scattering techniques use beams of neutrons. In that case the scattering interaction is between the magnetic moments of the incident neutrons and nuclei in the solid, but the principles are the same as for x-ray diffraction. Of course, it is the wave character of neutrons (in particular, their de Broglie wavelength; see Chapter 4) that is responsible for neutron diffraction. Recall that the de Broglie wavelength and neutron momentum are related by $\lambda = h/p$.

FIGURE 21.11 Constructive interference of x-rays scattered by atoms in lattice planes. Three beams of x-rays, scattered by atoms in three successive layers of a simple cubic crystal, are shown. Note that the phases of the waves are the same along the line CH, indicating constructive interference at this scattering angle 2θ.



EXAMPLE 21.2

A diffraction pattern of aluminum is obtained by using x-rays with wavelength $\lambda = 0.709$ Å. The second-order Bragg diffraction from the parallel faces of the cubic unit cells is observed at the angle $2\theta = 20.2°$. Calculate the lattice parameter a.

SOLUTION

From the Bragg condition for $n = 2$,

$$2\lambda = 2d \sin \theta$$

the spacing between planes, which is the lattice parameter, is

$$d = \frac{\lambda}{\sin \theta} = \frac{0.709 \text{ Å}}{\sin (10.1°)} = 4.04 \text{ Å} = a$$

Related Problems: 5, 6

21.2 Crystal Structure

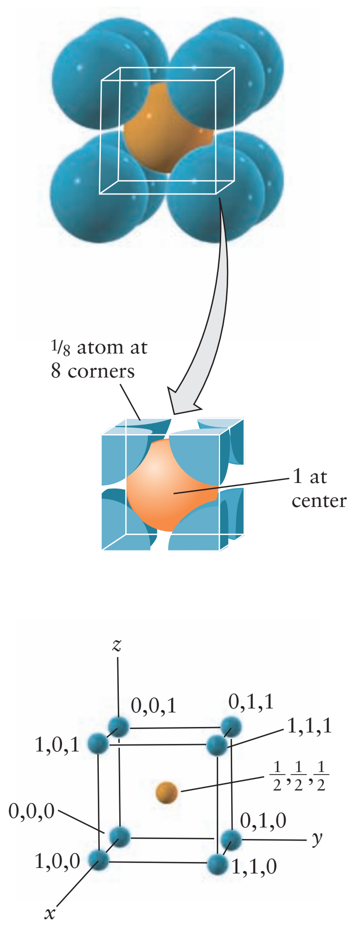


FIGURE 21.12 The bcc structure. An atom is located at the center of each cubic cell (orange) as well as at each corner of the cube (blue). The atoms are reduced slightly in size to make positions clear.

The crystal lattice is an abstract construction whose points of intersection describe the underlying symmetry of a crystal. To flesh out the description of a particular solid state structure, we must identify some structural elements that are "pinned" to the lattice points. These structural elements can be atoms, ions, or even groups of atoms as we see in this and the next chapter. We begin with some illustrative simple cases. Some of the chemical elements crystallize in particularly simple solid structures, in which a single atom is situated at each point of the lattice.

Polonium is the only element known to crystallize in the **simple cubic lattice,** with its atoms at the intersections of three sets of equally spaced planes that meet at right angles. Each unit cell contains one Po atom, separated from each of its six nearest neighbors by 3.35 Å.

The alkali metals crystallize in the **body-centered cubic (bcc) structure** at atmospheric pressure (Fig. 21.12). A unit cell of this structure contains two lattice points, one at the center of the cube and the other at any one of the eight corners. A single alkali-metal atom is associated with each lattice point. An alternative way to visualize this is to realize that each of the eight atoms that lie at the corners of a bcc unit cell is shared by the eight unit cells that meet at those corners. The contribution of the atoms to one unit cell is therefore $8 \times \frac{1}{8} = 1$ atom, to which is added the atom that lies wholly within that cell at its center.

The metals aluminum, nickel, copper, and silver, among others, crystallize in the **face-centered cubic (fcc) structure** shown in Figure 21.13. This unit cell contains four lattice points, with a single atom associated with each point. No atom lies wholly within the unit cell; there are atoms at the centers of its six faces, each of which is shared with another cell (contributing $6 \times \frac{1}{2} = 3$ atoms), and an atom at each corner of the cell (contributing $8 \times \frac{1}{8} = 1$ atom), for a total of four atoms per unit cell.

The volume of a unit cell is given by the formula

$$V_c = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma} \qquad [21.2]$$

When the angles are all 90° (so that their cosines are 0), this formula reduces to the simple result $V = abc$ for the volume of a rectangular box. If the mass of the unit cell contents is known, the theoretical cell density can be computed. This density must come close to the measured density of the crystal, a quantity that can be determined by entirely independent experiments. For an *element* whose crystal contains n_c atoms per unit cell, the calculated cell density is

$$\text{density} = \rho = \frac{\text{mass}}{\text{volume}} = \frac{n_c \dfrac{\mathcal{M}}{\mathrm{N_A}}}{V_c} = \frac{n_c \mathcal{M}}{\mathrm{N_A} V_c}$$

where we have used the fact that the molar mass $\mathcal{M}$ of the element divided by Avogadro's number $\mathrm{N_A}$ is the mass of a single atom. This equation can also be used to calculate Avogadro's number from the measured density and cell constants, as the following example illustrates.

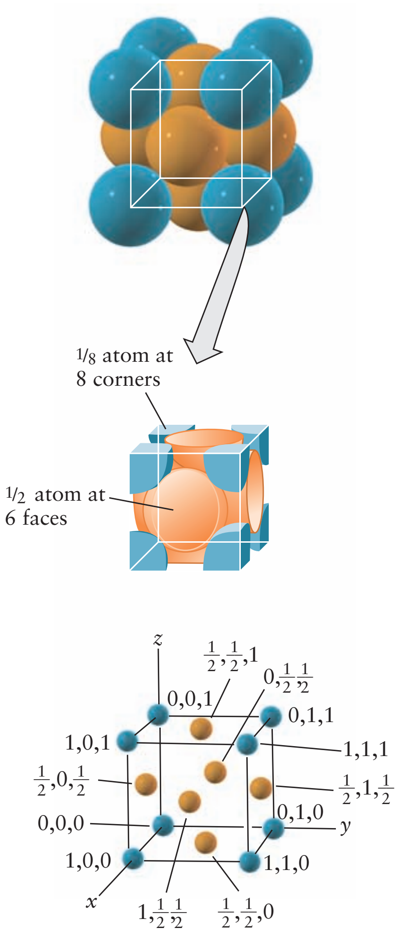


FIGURE 21.13 The fcc structure. Atoms are located at the centers of the faces (orange) as well as at the corners of the cube (blue). The atoms are reduced slightly in size to make positions clear.

EXAMPLE 21.3

Sodium has a density of $\rho = 0.9700 \text{ g cm}^{-3}$ at 20°C, and its lattice parameter is $a = 4.2856$ Å. What is the value of Avogadro's number, given that the molar mass of sodium is $22.9898 \text{ g mol}^{-1}$?

SOLUTION

Sodium has two atoms per unit cell because its structure is bcc, and the volume of the unit cell is a^3. Solve the foregoing equation for Avogadro's number:

$$\mathrm{N_A} = \frac{n_c \mathcal{M}}{\rho a^3} = \frac{(2)(22.9898 \text{ g mol}^{-1})}{(0.9700 \text{ g cm}^{-3})(4.2856 \times 10^{-8} \text{ cm})^3} = 6.022 \times 10^{23} \text{ mol}^{-1}$$

Related Problems: 15, 16

It is useful to define the locations of atoms in the unit cell with a set of three numbers measured in units of the lattice parameter(s). For this purpose, one corner of the unit cell is taken to be at the origin of the coordinate axes appropriate to the crystal system, and an atom at that lattice point has the coordinates (0, 0, 0). Equivalent atoms at the seven remaining corners of the cell then have the coordinates (1, 0, 0), (0, 1, 0), (0, 0, 1), (1, 0, 1), (1, 1, 0), (0, 1, 1), and (1, 1, 1). These atom positions are generated from an atom at (0, 0, 0) by successive translations through unit distances along the three axes. An atom in a body-centered site has coordinates $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and the prescription for locating it is to proceed from the coordinate origin at (0, 0, 0) a distance $a/2$ along a, then a distance $b/2$ along b, and finally $c/2$ along c. In the same way, an atom in a face-centered site has coordinates such as $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, or $(0, \frac{1}{2}, \frac{1}{2})$.

So far, we have considered only cubic metals in which one atom corresponds to each lattice point. More complicated structures also occur, even for the elements, in which atoms occupy positions that are not lattice points. Diamond has an fcc structure with eight atoms (not four) per unit cell (See Fig. 21.22). Boron has a tetragonal structure with a very complex unit cell that contains 50 atoms. In molecular crystals the number of atoms per unit cell can be still greater; in a protein with a molecular mass of 10^5, there may be tens of thousands of atoms per unit cell. The protein shown in Figure 23.13 is an example of a complex structure revealed by modern x-ray crystallography.

Atomic Packing in Crystals

As we begin to add structural features like atoms onto crystal lattice sites, we have to pay attention to the size of the features. How efficiently can we pack atoms onto a lattice? We have already discussed two measures of the "size" of an atom or molecule. In Section 9.7, the van der Waals parameter b was related to the volume excluded per mole of molecules, so $b/\mathrm{N_A}$ is one measure of molecular size. In

Section 5.5, we defined an approximate radius of an atom as the distance at which the electron density had fallen off to a particular value, or as the radius of a sphere containing a certain fraction of the total electron density. A third related measure of atomic size is based on the interatomic separations in a crystal. The radius of a noble-gas or metallic atom can be approximated as half the distance between the center of an atom and the center of its nearest neighbor in the crystal. We picture crystal structures as resulting from packing spheres in which nearest neighbors are in contact.

The nearest neighbor separation in a simple cubic crystal is equal to the lattice parameter a, so the atomic radius in that case is $a/2$. For the bcc lattice, the central atom in the unit cell "touches" each of the eight atoms at the corners of the cube, but those at the corners do not touch one another, as Figure 21.12 shows. The nearest neighbor distance is calculated from the Cartesian coordinates of the atom at the origin (0, 0, 0) and that at the cell center ($a/2$, $a/2$, $a/2$). By the Pythagorean theorem, the distance between these points is $\sqrt{(a/2)^2 + (a/2)^2 + (a/2)^2} = a\sqrt{3}/2$, so the atomic radius is $a\ \sqrt{3}/4$. Figure 21.13 shows that in an fcc crystal the atom at the center of a face [such as at (0, $a/2$, $a/2$)] touches each of the neighboring corner atoms [such as at (0, 0, 0)], so the nearest-neighbor distance is $\sqrt{(a/2)^2 + (a/2)^2} = a\ \sqrt{2}/2$ and the atomic radius is $a\ \sqrt{2}/4$. Table 21.2 summarizes the results for cubic lattices.

What is the most dense crystal packing that can be achieved? To answer this question, construct a crystal by first putting down a plane of atoms with the highest possible density, shown in Figure 21.14a. Each sphere is in contact with six other spheres in the plane. Then put down a second close-packed plane on top of the first one (see Fig. 21.14b) in such a way that each sphere in the second plane is in contact with three spheres in the plane below it; that is, each sphere in the second plane forms a tetrahedron with three spheres beneath. When the third plane is laid down, there are two possibilities. In Figure 21.14c, the atoms in the third plane lie on sites not directly over those in the first layer, whereas in Figure 21.14d the third-plane atoms are directly over the first-plane atoms.

TABLE 21.2 Structural Properties of Cubic Lattices

	Simple Cubic	Body-Centered Cubic	Face-Centered Cubic
Lattice points per cell	1	2	4
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	A	$a\sqrt{3}/2 = 0.866a$	$a\sqrt{2}/2 = 0.707a$
Atomic radius	$a/2$	$a\sqrt{3}/4 = 0.433a$	$a\sqrt{2}/4 = 0.354a$
Packing fraction	$\frac{\pi}{6} = 0.524$	$\frac{\sqrt{3}\pi}{8} = 0.680$	$\frac{\sqrt{2}\pi}{6} = 0.740$

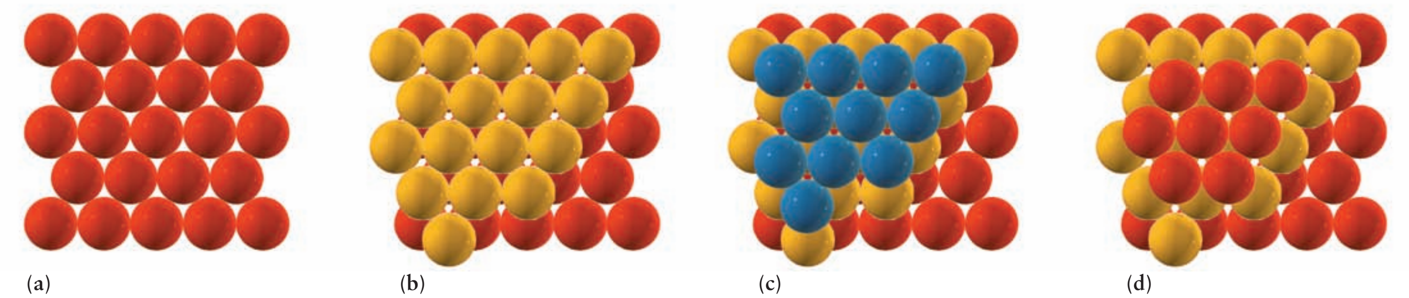

(a) (b) (c) (d)

FIGURE 21.14 Close-packing of spheres. (a) One layer, with each atom surrounded by six nearest neighbors. (b) Two layers, with the atoms of the second layer centered on top of indentations in the layer below. (c) The third layer can be placed on sites that are not directly above the sites in the first layer (note that the red spheres show through). If this pattern is repeated as *abcabc* . . . it gives cubic close-packing. (d) Alternatively, the third layer can be placed directly over the sites in the first layer (note that the white triangular spaces show through). The repeated pattern *ababab* . . . gives hexagonal close-packing.

Clearly, there are two choices for placing each plane, and an infinite number of crystal structures can be generated that have the same atomic packing density. The two simplest such structures correspond to the periodic layer sequences *abcabcab* . . . and *abababa*. . . . The first of these is the fcc structure already discussed, and the second is a close-packed structure in the hexagonal crystal system termed **hexagonal close-packed (hcp).** In each of these simple structures, atoms occupy 74.0% of the unit cell volume, as the following example shows. (Atoms that crystallize in the bcc structure occupy only 68.0% of the crystal volume, and the packing fraction for a simple cubic array is only 52.4%.)

EXAMPLE 21.4

Calculate (**a**) the atomic radius of an aluminum atom and (**b**) the fraction of the volume of aluminum that is occupied by its atoms.

SOLUTION

(**a**) Aluminum crystallizes in the fcc crystal system, and its unit cell therefore contains four atoms. Because a face-centered atom touches each of the atoms at the corners of its face, the atomic radius r_1 (see the triangle in Fig. 21.15) can be expressed by

$$4r_1 = a\sqrt{2}$$

Using the value $a = 4.04$ Å derived from x-ray diffraction (see Example 21.2) and solving for r_1 gives

$$r_1 = 1.43 \text{ Å}$$

(**b**) The fraction of the volume of an aluminum single crystal that is occupied by its atoms is

$$f = \frac{4\left[\frac{4}{3}\pi r_1^3\right]}{a^3} = \frac{4\frac{4}{3}\pi\left[\frac{a\sqrt{2}}{4}\right]^3}{a^3} = 0.740$$

Related Problem: 23

Interstitial Sites

The ways in which the empty volume is distributed in a crystal are both interesting and important. For the close-packed fcc structure, two types of **interstitial sites,** upon which the free volume in the unit cell is centered, are identifiable. An **octahedral site** is surrounded at equal distances by six nearest neighbor atoms. Figure 21.15 shows that such sites lie at the midpoints of the edges of the fcc unit cell. A cell has 12 edges, each of which is shared by four unit cells, so the edges contribute three octahedral interstitial sites per cell. In addition, the site at the center of the unit cell is also octahedral, so the total number of octahedral sites per fcc unit cell is four, the same as the number of atoms in the unit cell.

With a bit of simple geometry, we can calculate the size of an octahedral site in an fcc structure or, more precisely, the radius r_2 of a smaller atom that would fit in the site without overlapping its neighboring atoms. Figure 21.15 represents a cell face in which the length of the diagonal is $4r_1$ and the length of the cell edge is $2r_1 + 2r_2$, where r_1 is the radius of the host atoms and r_2 is the radius of the octahedral site. From the figure,

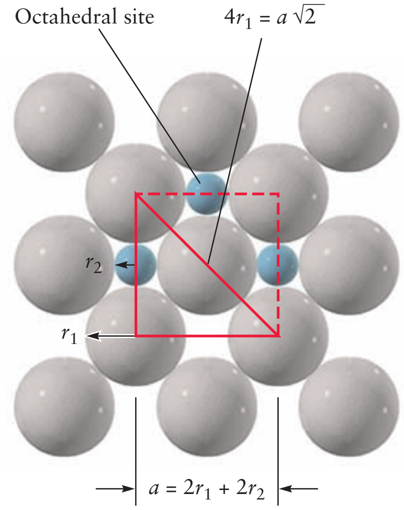


FIGURE 21.15 Octahedral sites in an fcc lattice. The geometric procedure for relating the site radius r_2 to the atom radius r_1 is shown.

$$r_1 = a\frac{\sqrt{2}}{4}$$

$$a = 2r_2 + 2r_1 = 2r_2 + 2a\frac{\sqrt{2}}{4}$$

$$r_2 = \frac{a}{2} - a\frac{\sqrt{2}}{4} = 0.146a$$

and the ratio of the octahedral-site radius to the host-atom radius is

$$\frac{r_2}{r_1} = \frac{0.146a}{a\sqrt{2}/4} = 0.414$$

The second type of interstitial site, known as a **tetrahedral site,** lies at the center of the space defined by four touching spheres. In an fcc cell, a tetrahedral site occurs in the volume between a corner atom and the three face-centered atoms nearest to it. Geometrical reasoning like that used for the octahedral site gives the following ratio of the radius of a tetrahedral site to that of a host atom:

$$\frac{r_2}{r_1} = 0.225$$

The fcc unit cell contains eight tetrahedral sites, twice the number of atoms in the cell.

Interstitial sites are important when a crystal contains atoms of several kinds with considerably different radii. We will return to this shortly when we consider the structures of ionic crystals.

21.3 Cohesion in Solids

In addition to symmetry, the nature of the bonding forces between atoms provides a useful way to classify solids. This classification does indeed lead to an understanding of the remarkable differences in the chemical and physical properties of different materials. We now consider crystals held together through ionic, metallic, or covalent bonding interactions, and the one class of solids held together by intermolecular forces.

Ionic Crystals

Compounds formed by atoms with significantly different electronegativities are largely ionic, and to a first approximation the ions can be treated as hard, charged spheres that occupy positions on the crystal lattice (see the ionic radii in Appendix F). All the elements of Groups I and II of the periodic table react with Group VI and VII elements to form ionic compounds, the great majority of which crystallize in the cubic system. The alkali-metal halides (except for the cesium halides), the ammonium halides, and the oxides and sulfides of the alkaline-earth metals all crystallize in the **rock-salt,** or **sodium chloride, structure** shown in Figure 21.16. It may be viewed as an fcc lattice of anions whose octahedral sites are all occupied by cations or, equivalently, as an fcc lattice of cations whose octahedral sites are

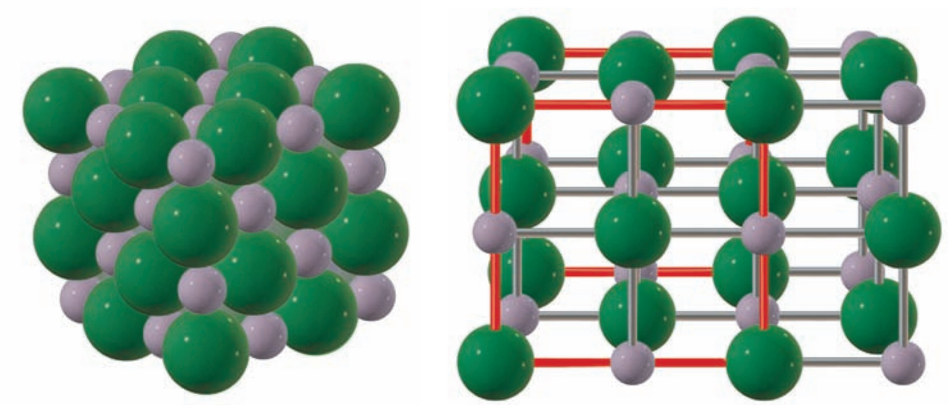


FIGURE 21.16 The sodium chloride, or rock-salt, structure. On the left, the sizes of the Na^+ ions (purplish pink) and the Cl^- ions (green) are drawn to scale. On the right, the ions are reduced in size to allow a unit cell (shown by red lines) to be outlined clearly.

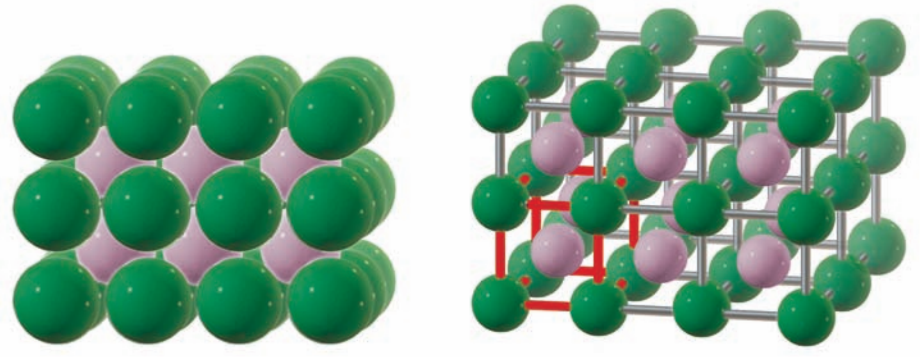
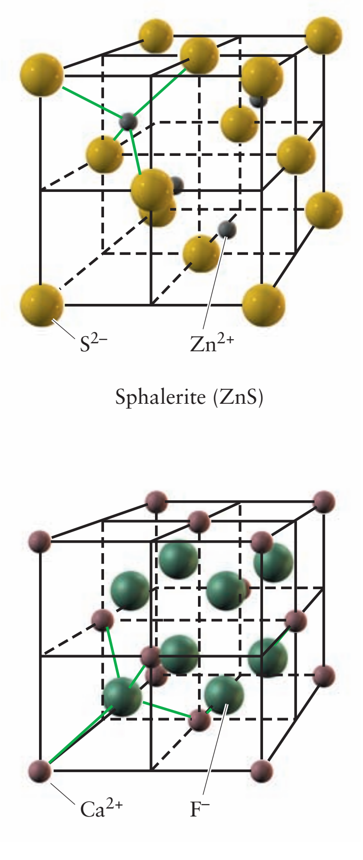


FIGURE 21.17 The structure of cesium chloride. On the left, the sizes of the Cs^+ ions (purplish pink) and the Cl^- ions (green) are drawn to scale. On the right, they are reduced in size to allow a unit cell (shown by red lines) to be outlined clearly. Note that the lattice in this structure is simple cubic, with one Cs^+ ion and one Cl^- ion per unit cell.

all occupied by anions. Either way, each ion is surrounded by six equidistant ions of the opposite charge. The rock-salt structure is a stable crystal structure when the cation-anion radius ratio lies between 0.414 and 0.732, if cations and anions are assumed to behave as incompressible charged spheres.

When the hard-sphere cation-anion radius ratio exceeds 0.732, as it does for the cesium halides, a different crystal structure called the **cesium chloride structure,** is more stable. It may be viewed as two interpenetrating simple cubic lattices, one of anions and the other of cations, as shown in Figure 21.17. When the cation–anion radius ratio is less than 0.414, the **zinc blende,** or **sphalerite, structure** (named after the structure of ZnS) results. This crystal consists of an fcc lattice of S^{2-} ions, with Zn^{2+} ions occupying half of the available tetrahedral sites in alternation, as Figure 21.18a illustrates. **Fluorite** (CaF_2) has yet another structure; the unit cell is based on an fcc lattice of Ca^{2+} ions. The F^- ions occupy all eight of the tetrahedral sites, so the unit cell contains four Ca^{2+} and eight F^- ions (see Fig. 21.18b). The radius ratios (0.414 and 0.732) at which crossovers from one type of crystal to another occur are not accidental numbers. Recall from Section 21.2 that 0.414 is the ratio of the octahedral-site radius to the host-atom radius for an fcc lattice; only when this size ratio is exceeded does the ion inserted into that site come into contact with ions of the opposite sign in the rock-salt structure. The number 0.732 comes from a corresponding calculation of the radius ratio of the interstitial site at the center of a simple cubic unit cell (see problem 25). It is important to realize that the radius-ratio criterion for the stability limits of the structures of binary ionic compounds assumes that the ions are incompressible and that the wave functions do not overlap. The criterion fails when these approximations are not met.

The strength and range of the electrostatic attractions make ionic crystals hard, high-melting, brittle solids that are electrical insulators. Melting an ionic crystal, however, disrupts the lattice and sets the ions free to move, so ionic liquids are good electrical conductors.



Sphalerite (ZnS)

Fluorite (CaF_2)

FIGURE 21.18 Two ionic lattices in the fcc system. A single (nonprimitive) cubic unit cell of each is shown.

Metallic Crystals

The type of bonding found in metals is quite different from that in other crystals. As we compare the various main group and transition metals in the periodic table we see only small differences in electronegativity. So, there is little tendency for ionic bonding in metals. The electronic configurations of metal atoms, even in the transition metals, do not have nearly-filled subshells, so there is little tendency to form covalent bonds by sharing electrons to achieve a stable octet. The familiar classical models of chemical bonding (see Chapter 3) do not extend to metals.

Prior to quantum mechanics, bonding in metals was described by the Drude model, named for the German physicist Paul Drude. The solid was viewed as a fixed array of positively charged metal ions, each localized at a site of the crystal lattice. These fixed ions were surrounded by a sea of mobile electrons, one contributed by each of the atoms in the solid. The number density of electrons was equal to the number density of positively charged ions, so the metal was electrically neutral. The sea of delocalized electrons would interact with the stable ions to give a strong cohesive force keeping the metal bound together. The Drude model accounts for the malleability (deformation in response to mechanical force, like hammering) and ductility (ease of drawing into a fine wire) of metals. As some ions move to new positions in response to these mechanical disturbances, delocalized electrons can rapidly adjust to maintain metallic bonding in the deformed or drawn solid. The ease with which metals conduct electricity is explained because these delocalized electrons can respond to any applied electric fields.

The delocalized sea of electrons picture of metal bonding survives in the quantum theory of solids, which is an extension of the molecular orbital description of molecular bonding (see Chapter 6). The valence electrons in a metal are delocalized in huge molecular orbitals that extend over the entire crystal and provide the "glue" that holds together the positively charged ion cores of the metal atoms. To understand the origin of these molecular orbitals, suppose just two sodium atoms are brought together, each in its electronic ground state with the configuration $1s^22s^22p^63s^1$. As the atoms approach each other, the wave functions of their 3*s* electrons combine to form two molecular orbitals—one in which their phases are symmetric (σ_{3s}) and another in which they are antisymmetric (σ_{3s}^*). Solving the Schrödinger equation yields two energy states, one above and the other below the energy of the atomic 3*s* levels, analogous to the formation of a hydrogen molecule from two hydrogen atoms described in Chapter 6. If both valence electrons are put into the level of lower energy with spins opposed, the result is a Na_2 molecule. If a third sodium atom is added, the 3*s* atomic levels of the atoms split into three sublevels (Fig. 21.19). Two electrons occupy the lowest level with their spins opposed, and the third electron occupies the middle level. The three energy levels and the three electrons belong collectively to the three sodium atoms. A fourth sodium atom could be added so that there would be four closely spaced energy sublevels, and this process could be carried on without limit.

The foregoing is not a mere "thought experiment." Sodium vapor contains about 17% Na_2 molecules at its normal boiling point. Larger sodium clusters have been produced in molecular beam experiments, and mass spectrometry shows that such clusters can contain any desired number of atoms. For each added Na atom, another energy sublevel is added. Because the sublevels are so very closely spaced in a solid (with, say, 10^{23} atoms), the collection of sublevels can be regarded as an **energy band.** Figure 21.19 depicts the formation of bands of sublevels that broaden (become delocalized) as the spacing between the nuclear centers decreases, and the 3*s* electrons go into these bands. The electrons that belong to the 1*s*, 2*s*, and 2*p* atomic levels of sodium are only very slightly broadened at the equilibrium internuclear separation of the crystal, so they retain their distinct, localized character as the core levels of the ions at the lattice sites. Chapter 22 explores the electrical properties of metals, which arise from this band structure.

Most metals have crystal structures of high symmetry and crystallize in bcc, fcc, or hcp lattices (Fig. 21.20). Relatively few metals (Ga, In, Sn, Sb, Bi, and Hg) have more complex crystal structures. Many metals undergo phase transitions to other structures when the temperature or pressure is changed. Both liquid and crystal phases can be metals; in fact, the conductivity usually drops by only a small amount when a metal melts. The electron sea provides very strong binding in most metals, as shown by their high boiling points. Metals have a very large range of melting points. Gallium melts at 29.78°C (Fig. 21.21), and mercury stays liquid at temperatures that freeze water. Many transition metals require temperatures in excess of 1000°C to melt, and tungsten, the highest melting elemental metal, melts at 3410°C (see Section 8.1).

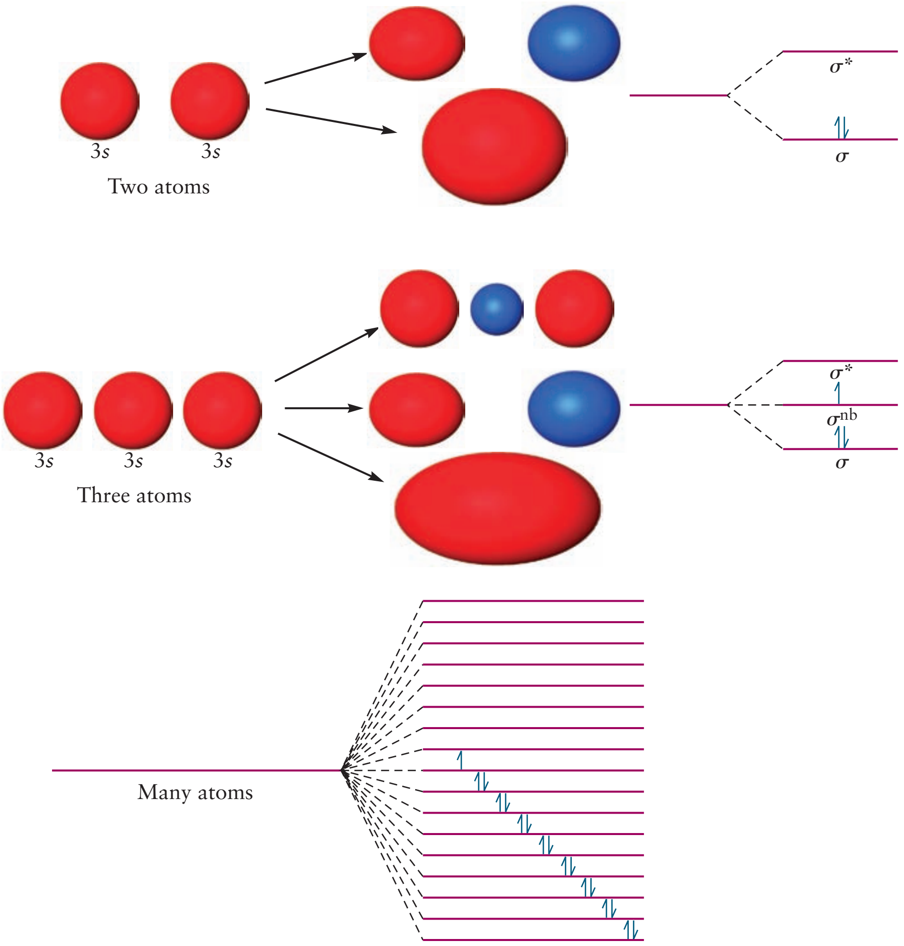


FIGURE 21.19 As sodium atoms are brought together, the molecular orbitals formed from their 3*s* atomic orbitals spread out into a band of levels, half occupied by electrons.

Covalent Crystals

We turn finally to a class of crystalline solids whose atoms are linked by covalent bonds rather than by the electrostatic attractions of ions or the valence electron "glue" in a metal. The archetype of the covalent crystal is diamond, which belongs to the cubic system. The ground-state electron configuration of a carbon atom is $1s^2 2s^2 2p^2$, and as shown in Section 6.5, its bonding is described by four hybrid sp^3 orbitals directed to the four corners of a regular tetrahedron. Each of the equivalent hybrid orbitals contains one electron that can spin-pair with the electron in one of the sp^3 orbitals of another carbon atom. Each carbon atom can thus link covalently to four others to yield the space-filling network shown in Figure 21.22. Covalent crystals are also called "network crystals," for obvious reasons. In a sense, every atom in a covalent crystal is part of one giant molecule that is the crystal itself. These crystals have very high melting points because of the strong attractions between covalently bound atoms. They are hard and brittle. Chapter 22 describes the electrical properties of covalent crystals.

Molecular Crystals

Molecular crystals include the noble gases; oxygen; nitrogen; the halogens; compounds such as carbon dioxide; metal halides of low ionicity such as Al_2Cl_6, $FeCl_3$, and $BiCl_3$; and the vast majority of organic compounds. All these molecules are held in their lattice sites by the intermolecular forces discussed in Sections 9.7 and 10.2. The trade-off between attractive and repulsive forces among even small mol-

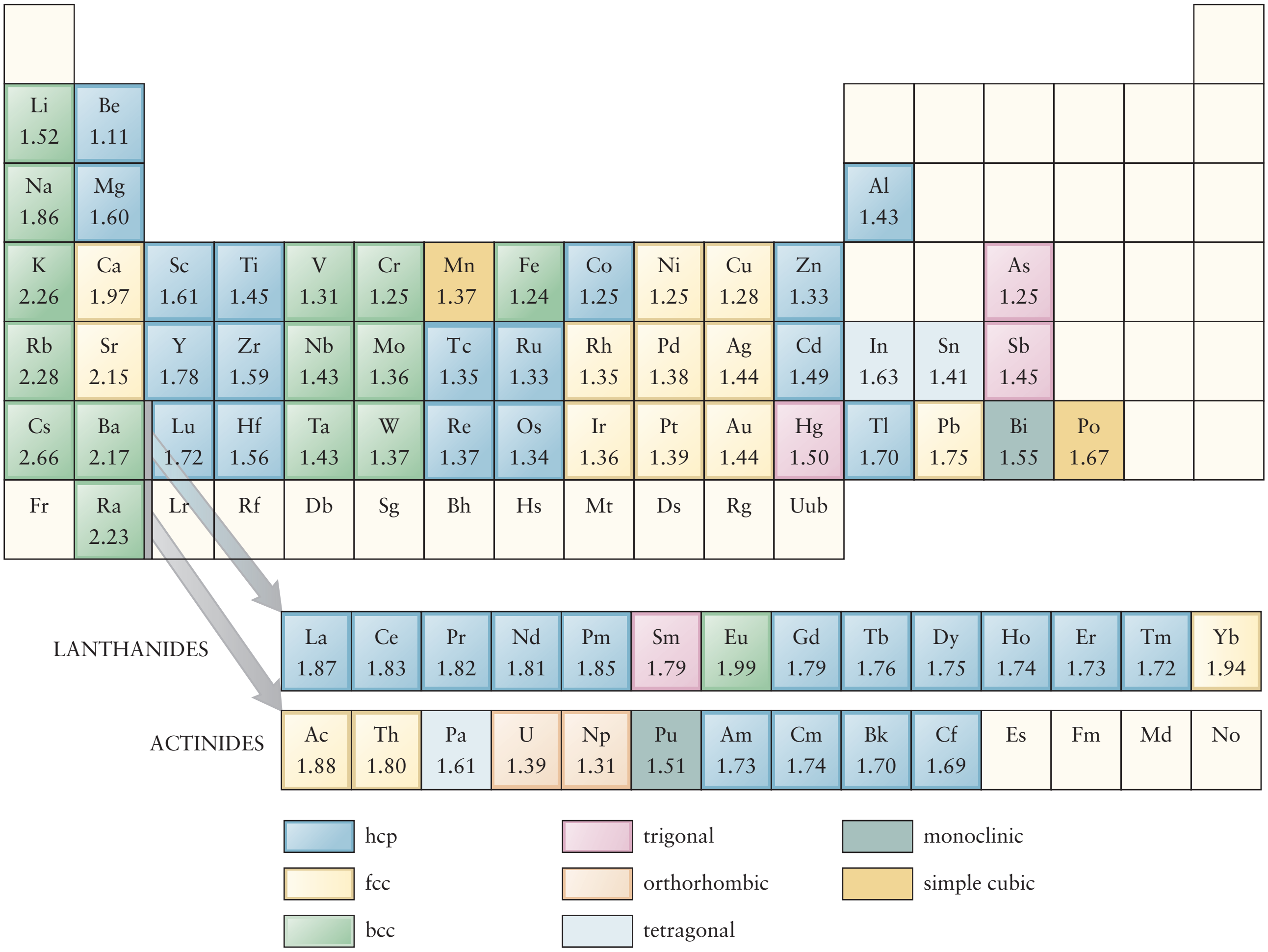


FIGURE 21.20 Crystal structures of the metallic elements at 25°C and 1 atm pressure. Atomic radii (Å) are calculated as one half the closest atom–atom distance in each structure; in most cases this is the same radius as calculated using the hard sphere contact model of Example 21.4. There are no known crystal structures for those elements for which atomic radii are not listed.

ecules in a molecular crystal is complex because so many atoms are involved. A useful simplification is to picture a molecule as a set of fused spheres centered at each nucleus. The radius of each sphere is the van der Waals radius of the element involved. In molecular crystals, such shapes pack together so that no molecules overlap but empty space is minimized. Figure 21.23 depicts such a "space-filling model" of cyanuric triazide (C_3N_{12}), showing how nature solves the problem of efficiently packing many copies of the rather complicated molecular shape of C_3N_{12} in a single layer. In the three-dimensional molecular crystal of C_3N_{12}, many such layers stack up with a slight offset that minimizes unfilled space between layers.

Van der Waals forces are much weaker than the forces that operate in ionic, metallic, and covalent crystals. Consequently, molecular crystals typically have low melting points and are soft and easily deformed. Although at atmospheric pressure the noble-gas elements crystallize in the highly symmetric fcc lattice shown in Figure 21.13, molecules (especially those with complex geometries) more often form crystals of low symmetry in the monoclinic or triclinic systems. Molecular crystals are of great scientific value. If proteins and other macromolecules are obtained in the crystalline state, their structures can be determined by x-ray diffraction. Knowing the three-dimensional structures of biological molecules is the starting point for understanding their functions.


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FIGURE 21.21 Solid gallium has a low melting point, low enough to melt from the heat of the body.

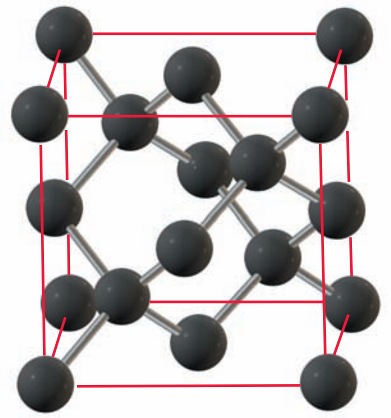


FIGURE 21.22 The structure of diamond. Each carbon atom has four nearest neighbors surrounding it at the corners of a tetrahedron.

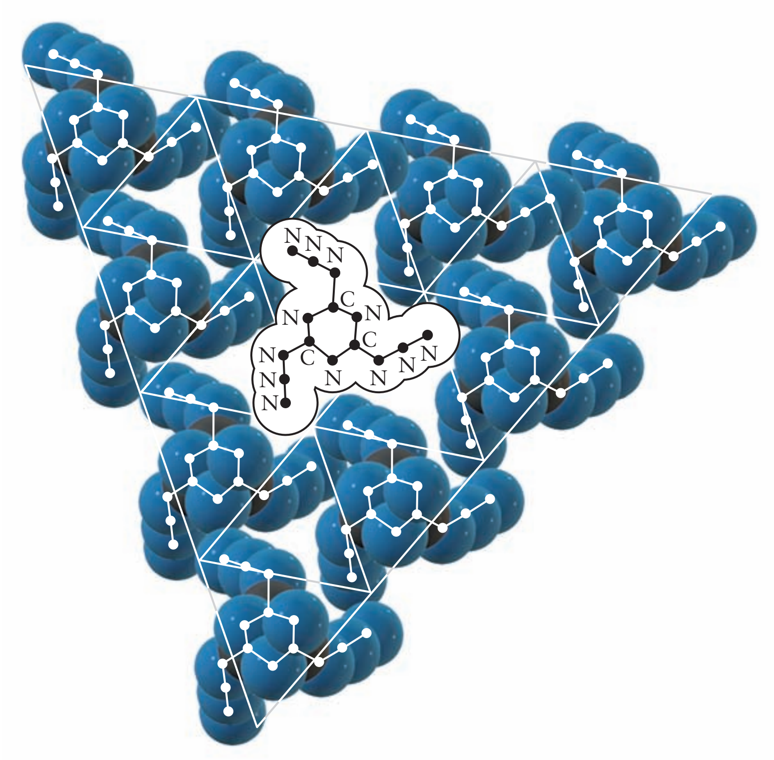
Crystal Structures of the Elements

The chemical elements provide examples of three of the four classes of crystalline solids described in this section. Only ionic solids are excluded, because a single element cannot have the two types of atoms of different electronegativities needed to form an ionic material. We have already discussed some of the structures formed by metallic elements, which are sufficiently electropositive that their atoms readily give up electrons to form the electron sea of metallic bonding. The nonmetallic elements are more complex in their structures, reflecting a competition between intermolecular and intramolecular bonding and producing molecular or covalent solids with varied properties.

Each halogen atom has seven valence electrons and can react with one other halogen atom to form a diatomic molecule. Once this single bond forms, there is no further bonding capacity; the halogen diatomic molecules interact with one another only through relatively weak van der Waals forces and form molecular solids with low melting and boiling points.

The Group VI elements oxygen, sulfur, and selenium display dissimilar structures in the solid state. Each oxygen atom (with six valence electrons) can form one double or two single bonds. Except in ozone, its high-free-energy form, oxygen uses up all its bonding capacity with an intramolecular double bond, forming a molecular liquid and a molecular solid that are only weakly bound. In contrast, diatomic sulfur molecules ($S{=}S$) are relatively rare, being encountered only in high-temperature vapors. The favored forms of sulfur involve the bonding of every atom to two other sulfur atoms. This leads to either rings or chains, and both are observed. The stable form of sulfur at room temperature consists of S_8 molecules, with eight sulfur atoms arranged in a puckered ring (Fig. 21.24). The weak interactions between S_8 molecules make elemental sulfur a rather soft molecular solid. Above 160°C the rings in molten sulfur break open and relink to form long, tangled chains, producing a highly viscous liquid. An unstable ring form of selenium (Se_8) is known, but the thermodynamically stable form of this element is a gray

FIGURE 21.23 The van der Waals radii of the carbon and nitrogen atoms superimposed on an outline of the molecular structure of cyanuric triazide, C_3N_{12}, to show the volume of space from which each molecule excludes the others. Van der Waals forces in the molecular crystal hold the molecules in contact in a pattern that minimizes empty space. The thin white lines emphasize the 3-fold symmetry of the pattern.



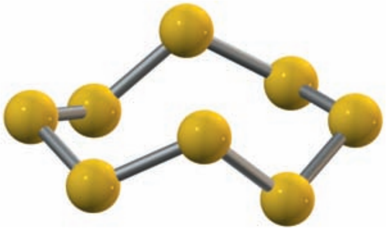


FIGURE 21.24 The structure of the S_8 sulfur molecule. The orthorhombic unit cell of rhombic sulfur, the most stable form of elemental sulfur at room temperature, is large and contains 16 of these S_8 molecules for a total of 128 atoms of sulfur.

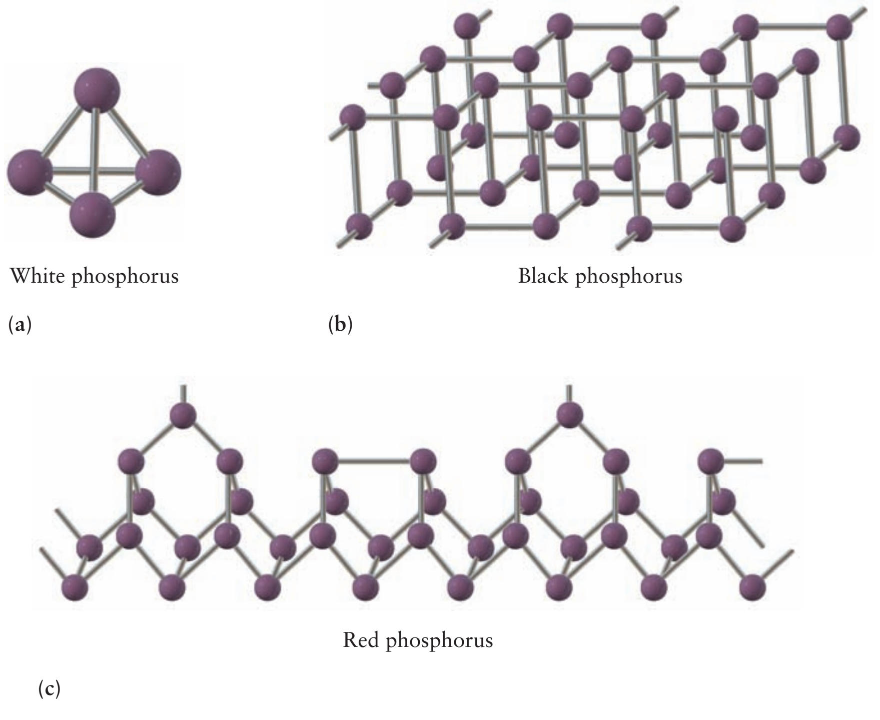
crystal of metallic appearance that consists of very long spiral chains with weak interchain interaction. Crystalline tellurium has a similar structure. The Group VI elements thus show a trend (moving down the periodic table) from the formation of multiple bonds toward the chains and rings characteristic of atoms that each form two single bonds.

A similar trend is evident in Group V. Only nitrogen forms diatomic molecules with triple bonds, in which all the bonding capacity is used between pairs of atoms. Elemental phosphorus exists in three forms, in all of which each phosphorus atom forms three single bonds rather than one triple bond. White phosphorus (Fig. 21.25a) consists of tetrahedral P_4 molecules, which interact with each other through weak van der Waals forces. Black phosphorus and red phosphorus (see Figs. 21.25b, c) are higher melting network solids in which the three bonds formed by each atom connect it directly or indirectly with all the other atoms in the sample. Unstable solid forms of arsenic and antimony that consist of As_4 or Sb_4 tetrahedra like those in white phosphorus can be prepared by rapid cooling of the vapor. The stable forms of these elements have structures related to that of black phosphorus.

The elements considered so far lie on the border between covalent and molecular solids. Other elements, those of intermediate electronegativity, exist as solids on the border between metallic and covalent; these are called **metalloids.** Antimony has a metallic luster, for example, but is a rather poor conductor of electricity and heat. Silicon and germanium are **semiconductors,** with electrical conductivities far lower than those of metals but still significantly higher than those of true insulators such as diamond. Section 22.7 examines the special properties of these materials more closely.

Some elements of intermediate electronegativity exist in two crystalline forms with very different properties. White tin has a tetragonal crystal structure and is a metallic conductor. Below 13°C it crumbles slowly to form a powder of gray tin (with the diamond structure) that is a poor conductor. Its formation at low temperature is known as the "tin disease" and can be prevented by the addition of

FIGURE 21.25 Structures of elemental phosphorus.



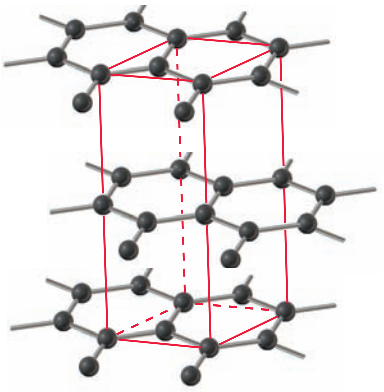


FIGURE 21.26 The structure of graphite.

small amounts of bismuth or antimony. The thermodynamically stable form of carbon at room conditions is not the insulator diamond, but graphite. Graphite consists of sheets of fused hexagonal rings with only rather weak interactions between layers (Fig. 21.26). Each carbon atom shows sp^2 hybridization, with its remaining p orbital (perpendicular to the graphite layers) taking part in extended π-bonding interactions over the whole plane. Graphite can be pictured as a series of interlocked benzene rings, with π-electron delocalization contributing significantly to its stability. The delocalized electrons give graphite a significant value for conductivity in the planes of fused hexagons approaching that of the metallic elements. The conductivity and relative chemical inertness of graphite make it useful for electrodes in electrochemistry.

A DEEPER LOOK

21.4 Lattice Energies of Crystals

The **lattice energy** of a crystal is the energy required to separate the crystal into its component atoms, molecules, or ions at 0 K. In this section we examine the calculation and measurement of lattice energies for molecular and ionic crystals.

Lattice Energy of a Molecular Crystal

The lattice energy of a molecular crystal can be estimated by using the simple Lennard-Jones potential of Section 9.7:

$$V_{\mathrm{LJ}}(R) = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$

Table 9.4 lists the values of e and σ for various atoms and molecules. To obtain the total potential energy for 1 mol, sum over all pairs of atoms or molecules:

$$V_{\mathrm{tot}} = \frac{1}{2}\sum_{i=1}^{N_{\mathrm{A}}}\sum_{j=1}^{N_{\mathrm{A}}} V_{\mathrm{LJ}}(R_{ij})$$

where R_{ij} is the distance between atom i and atom j. The factor $\frac{1}{2}$ arises because each interaction between a pair of atoms should be counted only once, not twice. For a crystal of macroscopic size, this can be rewritten as

$$V_{\mathrm{tot}} = \frac{N_{\mathrm{A}}}{2}\sum_{j=1}^{N_{\mathrm{A}}} V_{\mathrm{LJ}}(R_{ij})$$

where i is taken to be some atom in the middle of the crystal. Taking the nearest neighbor distance to be R_0, we define a ratio of distances $p_{ij} = R_{ij}/R_0$ and rewrite V_{tot} for the Lennard-Jones potential as

$$\begin{aligned} V_{\mathrm{tot}} &= \frac{N_{\mathrm{A}}}{2}(4\varepsilon)\left[\sum_j\left(\frac{\sigma}{p_{ij}R_0}\right)^{12} - \sum_j\left(\frac{\sigma}{p_{ij}R_0}\right)^{6}\right] \\ &= 2\varepsilon N_{\mathrm{A}}\left[\left(\frac{\sigma}{R_0}\right)^{12}\sum_j (p_{ij})^{-12} - \left(\frac{\sigma}{R_0}\right)^{6}\sum_j (p_{ij})^{-6}\right] \end{aligned}$$

The two summations are dimensionless properties of the lattice structure, and accurate values can be obtained by summing over the first few sets of nearest neighbors (Table 21.3). The resulting total energy for the fcc lattice is

$$V_{\mathrm{tot}} = 2\varepsilon N_{\mathrm{A}}\left[12.132\left(\frac{\sigma}{R_0}\right)^{12} - 14.454\left(\frac{\sigma}{R_0}\right)^{6}\right]$$

The equilibrium atomic spacing at $T = 0$ K should be close to the one that gives a minimum in V_{tot}, which can be calculated by differentiating the preceding expression with respect to R_0 and setting the derivative to 0. The result is

$$R_0 = 1.09\sigma$$

and the value of V_{tot} at this value of R_0 is

$$V_{\mathrm{tot}} = -8.61\varepsilon N_{\mathrm{A}}$$

The corresponding potential energy when the atoms or molecules are completely separated from one another is zero. The

TABLE 21.3 Lattice Sums for Molecular Crystals (fcc Structure)

	Number, n	p_{ij}	$n(p_{ij})^{-12}$	$n(p_{ij})^{-6}$
Nearest neighbors	12	1	12	12
Second nearest neighbors	6	$\sqrt{2}$	0.0938	0.750
Third nearest neighbors	24	$\sqrt{3}$	0.0329	0.889
Fourth nearest neighbors	12	2	0.0029	0.188
Fifth nearest neighbors	24	$\sqrt{5}$	0.0015	0.192
	⋮	⋮	⋮	⋮
Total			12.132	14.454

TABLE 21.4 Properties of Noble-Gas Crystals[†]

	R_0 (Å)		Lattice Energy (kJ mol^{-1})	
	Predicted	Observed	Predicted	Observed
Ne	3.00	3.13	1.83	1.88
Ar	3.71	3.76	7.72	7.74
Kr	3.92	4.01	11.50	11.20
Xe	4.47	4.35	15.20	16.00

[†] All data are extrapolated to 0 K and zero pressure.

lattice energy is the difference between these quantities and is a positive number:

$$\text{lattice energy} = -V_{\text{tot}} = 8.61\varepsilon N_{\text{A}}$$

This overestimates the true lattice energy because of the quantum effect of zero-point energy (see Sections 4.6 and 4.7). When a quantum correction is applied, the binding energy is reduced by 28%, 10%, 6%, and 4% for Ne, Ar, Kr, and Xe, respectively. Table 21.4 shows the resulting predictions for crystal lattice energies and nearest neighbor distances. The agreement with experiment is quite reasonable, considering the approximations inherent in the use of a Lennard–Jones potential derived entirely from gas-phase data. For helium the amplitude of zero-point motion is so great that if a crystal did form, it would immediately melt. Consequently, helium remains liquid down to absolute zero at atmospheric pressure.

Lattice Energy of an Ionic Crystal

In Section 3.6, we calculated the potential energy of a gaseous diatomic ionic molecule relative to the separated ions by means of Coulomb's law:

$$V = \frac{q_1 q_2}{4\pi\epsilon_0 R_0}$$

where R_0 is the equilibrium internuclear separation. Coulomb's law can also be used to calculate the lattice energies of ionic compounds in the crystalline state.

For simplicity, consider a hypothetical one-dimensional crystal (Fig. 21.27), in which ions of charge $+e$ and $-e$ alternate with an internuclear separation of R_0. One ion, selected to occupy an arbitrary origin, will interact attractively with all ions of opposite sign to make the following contribution to the crystal energy:

$$V_{\text{attraction}} = -\frac{e^2}{4\pi\epsilon_0 R_0}\left[2(1) + 2(\tfrac{1}{3}) + 2(\tfrac{1}{5}) + \ldots\right]$$

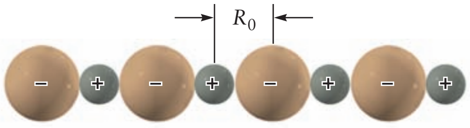


FIGURE 21.27 Lattice energy for a one-dimensional ionic crystal.

Here the factors of 2 come from the fact that there are *two* ions of opposite sign at a distance R_0 from a given ion, two at a distance $3R_0$, two at $5R_0$, and so forth. The negative sign occurs because the ions that occupy odd-numbered sites have a charge opposite that of the ion at the origin, and their interaction with the ion at the origin is attractive. The ion at the origin also interacts repulsively with all ions of the same sign to make the following contribution to the crystal energy:

$$V_{\text{repulsion}} = +\frac{e^2}{4\pi\epsilon_0 R_0}\left[2(\tfrac{1}{2}) + 2(\tfrac{1}{4}) + 2(\tfrac{1}{6}) + \ldots\right]$$

The net interaction of N_{A} such ions of each sign with one another is:

$$V_{\text{net}} = -\frac{N_{\text{A}} e^2}{4\pi\epsilon_0 R_0}\left[2 - \frac{2}{2} + \frac{2}{3} - \frac{2}{4} + \frac{2}{5} - \frac{2}{6} + \ldots\right]$$

We must be very careful with factors of 2. To obtain the potential energy for the interaction of N_{A} positive ions with N_{A} negative ions, it is necessary to multiply the total potential energy of a given ion due to all others by $2N_{\text{A}}$ and then divide by 2 to avoid counting the interaction of a given pair of ions twice. This gives the preceding result.

If such a calculation is carried out for a real three-dimensional crystal, the result is a series (such as that just given in brackets) whose value sums to a dimensionless number that depends upon the crystal structure. That number is called the **Madelung constant,** M, and its value is independent of the unit-cell dimensions. Table 21.5 lists the values of the Madelung constant for several crystal structures. The lattice energy is again the opposite of the total potential energy. Expressed in terms of the Madelung constant, it is

$$\boxed{\text{lattice energy} = \frac{N_{\text{A}} e^2}{4\pi\epsilon_0 R_0} M} \qquad [21.3]$$

TABLE 21.5 Madelung Constants

Lattice	*M*
Rock salt	1.7476
CsCl	1.7627
Zinc blende	1.6381
Fluorite	2.5194

EXAMPLE 21.5

Calculate the electrostatic part of the lattice energy of sodium chloride, given that the internuclear separation between Na^+ and Cl^- ions is 2.82 Å.

SOLUTION

Using the Madelung constant of 1.7476 for this structure gives

$$\frac{(6.02 \times 10^{23}\ \text{mol}^{-1})(1.602 \times 10^{-19}\ \text{C})^2(1.7476)}{(4\pi)(8.854 \times 10^{-12}\ \text{C}^2\ \text{J}^{-1}\ \text{m}^{-1})(2.82 \times 10^{-10}\ \text{m})} =$$

$$8.61 \times 10^5\ \text{J mol}^{-1} = 861\ \text{kJ mol}^{-1}$$

Related Problems: 35, 36

Ionic lattice energies are measured experimentally by means of a thermodynamic cycle developed by Max Born and Fritz Haber. The **Born–Haber cycle** is an application of Hess's law (the first law of thermodynamics). It is illustrated by a determination of the lattice energy of sodium chloride, which is ΔE for the reaction

$$\text{NaCl}(s) \longrightarrow \text{Na}^+(g) + \text{Cl}^-(g) \qquad \Delta E = ?$$

This reaction can be represented as a series of steps, each with a measurable energy or enthalpy change. In the first step, the ionic solid is converted to the elements in their standard states:

$$\text{NaCl}(s) \longrightarrow \text{Na}(s) + \tfrac{1}{2}\,\text{Cl}_2(g)$$

$$\Delta E_1 \approx \Delta H = -\Delta H_f^\circ(\text{NaCl}(s)) = +411.2\ \text{kJ}$$

In the second step, the elements are transformed into gas-phase atoms:

$$\text{Na}(s) \longrightarrow \text{Na}(g) \qquad \Delta E \approx \Delta H = \Delta H_f^\circ(\text{Na}(g)) = +107.3\ \text{kJ}$$

$$\tfrac{1}{2}\,\text{Cl}_2(g) \longrightarrow \text{Cl}(g) \qquad \Delta E \approx \Delta H = \Delta H_f^\circ(\text{Cl}(g)) = +121.7\ \text{kJ}$$

$$\text{Na}(s) + \tfrac{1}{2}\,\text{Cl}_2(g) \longrightarrow \text{Na}(g) + \text{Cl}(g) \qquad \Delta E_2 = +229.0\ \text{kJ}$$

Finally, in the third step, electrons are transferred from the sodium atoms to the chlorine atoms to give ions:

$$\text{Na}(g) \longrightarrow \text{Na}^+(g) + e^- \qquad \Delta E = IE_1(\text{Na}) = 496\ \text{kJ}$$

$$\text{Cl}(g) + e^- \longrightarrow \text{Cl}^-(g) \qquad \Delta E = -EA(\text{Cl}) = -349\ \text{kJ}$$

$$\text{Na}(g) + \text{Cl}(g) \longrightarrow \text{Na}^+(g) + \text{Cl}^-(g) \qquad \Delta E_3 = +147\ \text{kJ}$$

Here $EA(\text{Cl})$ is the electron affinity of Cl, and $IE_1(\text{Na})$ is the first ionization energy of Na. The total energy change is

$$\Delta E = \Delta E_1 + \Delta E_2 + \Delta E_3 = 411 + 229 + 147 = +787\ \text{kJ}$$

The small differences between ΔE and ΔH were neglected in this calculation. If their difference is taken into account (using $\Delta H = \Delta E + RT\Delta n_g$, where Δn_g is the change in the number of moles of gas molecules in each step of the reaction), then ΔE_2 is decreased by $\frac{3}{2}RT$ and ΔE_1 by $\frac{1}{2}RT$, giving a net decrease of $2RT$ and changing ΔE to $+782\ \text{kJ mol}^{-1}$. Comparing this experimental lattice energy with the energy calculated in Example 21.5 shows that the latter is approximately 10% greater, presumably because short-range repulsive interactions and zero-point energy were not taken into account in the lattice energy calculation.

21.5 Defects and Amorphous Solids

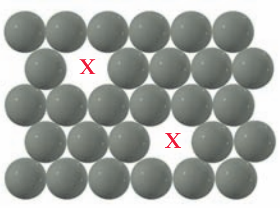
Although real crystals display beautiful symmetries to the eye, they are not perfect. As a practical matter, it is impossible to rid a crystal of all impurities or to ensure that it contains perfect periodic ordering. So, we describe real crystals as "perfect crystals with defects," and define means to characterize these defects. If so many defects are present that crystalline order is destroyed, we describe the material as an **amorphous solid.**

Point Defects

Point defects in a pure crystalline substance include **vacancies,** in which atoms are missing from lattice sites, and **interstitials,** in which atoms are inserted in sites different from their normal sites. In real crystals, a small fraction of the normal atom sites remain unoccupied. Such vacancies are called **Schottky defects,** and their concentration depends on temperature:

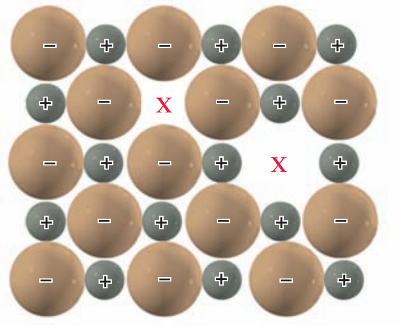
$$N = N_s \exp(-\Delta G/RT)$$

where N is the number of lattice vacancies per unit volume, N_s is the number of atom sites per unit volume, and ΔG is the molar free energy of formation of



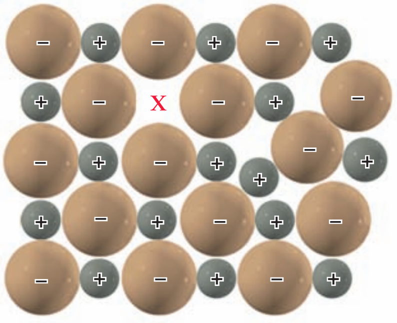
Schottky defects in a metal or noble gas crystal

(a)



Schottky defects in an ionic crystal

(b)



Frenkel defect in an ionic crystal

(c)

FIGURE 21.28 Point imperfections in a lattice. The red Xs denote vacancies.

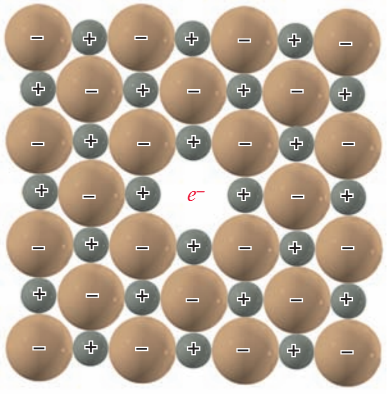


FIGURE 21.29 An F-center in a crystal.

vacancies. Figure 21.28a illustrates Schottky defects in the crystal structure of a metal or noble gas. Schottky defects also occur in ionic crystals but with the restriction that the imperfect crystals remain electrically neutral. Thus, in sodium chloride, for every missing Na^+ ion there must also be a missing Cl^- ion (see Fig. 21.28b).

In certain kinds of crystals, atoms or ions are displaced from their regular lattice sites to interstitial sites, and the crystal defect consists of the lattice vacancy plus the interstitial atom or ion. Figure 21.28c illustrates this type of lattice imperfection, known as a **Frenkel defect.** The silver halides (AgCl, AgBr, AgI) are examples of crystals in which Frenkel disorder is extreme. The crystal structures of these compounds are established primarily by the anion lattice, and the silver ions occupy highly disordered, almost random, sites. The rate of diffusion of silver ions in these solids is exceptionally high, as studies using radioactive isotopes of silver have shown. Both Frenkel and Schottky defects in crystals are mobile, jumping from one lattice site to a neighboring site with frequencies that depend on the temperature and the strengths of the atomic forces. Diffusion in crystalline solids is due largely to the presence and mobility of point defects; it is a thermally activated process, just like the rates of chemical reactions considered in Chapter 18. The coefficient of self-diffusion has the form

$$D = D_0 \exp[-E_a/RT] \tag{21.4}$$

where E_a is the activation energy. The rates of diffusive motion in crystalline solids vary enormously from one substance to another. In a crystal of a low-melting metal such as sodium, an average atom undergoes about 10^8 diffusive jumps per second at 50°C, whereas in a metal such as tungsten that melts at 3410°C, an average atom jumps to another lattice site less than once per year at 1000°C!

If an alkali halide crystal such as NaCl is irradiated with x-rays, ultraviolet radiation, or high-energy electrons, some Cl^- ions may lose an electron:

$$Cl^- + h\nu \longrightarrow Cl + e^-$$

The resulting Cl atom, being uncharged and much smaller than a Cl^- ion, is no longer strongly bound in the crystal and can diffuse to the surface and escape. The electron can migrate through the crystal quite freely until it encounters an anion vacancy and is trapped in the Coulomb field of the surrounding cations (Fig. 21.29). This crystal defect is called an **F-center** (from the German word *Farbenzentrum,* meaning **color center**). It is the simplest of a family of electronic crystal defects. As the name suggests, it imparts a color to ionic crystals (Fig. 21.30).

Nonstoichiometric Compounds

As Chapter 1 emphasizes, the law of definite proportions was one of the principal pieces of evidence that led to the acceptance of Dalton's atomic theory. It is now recognized that a great many solid-state binary compounds do *not* have fixed and unvarying compositions but exist over a range of compositions in a single phase. Thus, FeO (wüstite) has the composition range $Fe_{0.85}O_{1.00}$ to $Fe_{0.95}O_{1.00}$ and is never found with its nominal 1:1 composition. The compounds NiO and Cu_2S also deviate considerably from their nominal stoichiometries.

The explanation depends on the existence of more than one oxidation state for the metal. In wüstite, iron can exist in either the +2 or the +3 oxidation state. Suppose a solid were to begin at the hypothetical composition of $Fe_{1.00}O_{1.00}$, with iron entirely in the +2 oxidation state. For every two Fe^{3+} ions introduced, three Fe^{2+} ions must be removed to maintain overall charge neutrality. The total number of moles of iron is then less than that in the ideal FeO stoichiometry. The departure from the nominal stoichiometry can be far more extreme than that found in wüstite. The composition of "TiO" ranges from $Ti_{0.75}O$ to $Ti_{1.45}O$. Nickel oxide varies only from $Ni_{0.97}O$ to NiO in composition, but the variation is accompanied by a dramatic change in properties. When the compound is prepared in the 1:1 composition, it is pale green and is an electrical insulator. When it is prepared in an excess of oxygen, it is black and conducts electricity fairly well. In the black material, a small fraction of Ni^{2+} ions are replaced by Ni^{3+} ions, and compensating vacancies occur at some nickel atom sites in the crystal.


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FIGURE 21.30 Pure calcium fluoride, CaF2, is white but the natural sample of calcium fluoride (fluorite) shown here is a rich purple because F-centers are present. These are lattice sites where the F^- anion is replaced by an electron only.

EXAMPLE 21.6

The composition of a sample of wüstite is $Fe_{0.930}O_{1.00}$. What percentage of the iron is in the form of iron(III)?

SOLUTION

For every 1.00 mol of oxygen atoms in this sample, there is 0.930 mol of iron atoms. Suppose y mol of the iron is in the +3 oxidation state and $0.930 - y$ is in the +2 oxidation state. Then the total positive charge from the iron (in moles of electron charge) is

$$+3y + 2(0.930 - y)$$

This positive charge must exactly balance the 2 mol of negative charge carried by the mole of oxygen atoms (recall that each oxygen atom has oxidation number −2). We conclude that

$$3y + 2(0.930 - y) = +2$$

Solving this equation for y gives

$$y = 0.140$$

The percentage of iron in the form of Fe^{3+} is then the ratio of this number to the total number of moles of iron, 0.930, multiplied by 100%:

$$\%\text{ iron in form of } Fe^{3+} = \frac{0.140}{0.930} \times 100\% = 15.1\%$$

Related Problems: 41, 42

Alloys

The nonstoichiometric compounds just described are ionic materials with compositional disorder. A related type of disorder is exhibited by an **alloy,** a mixture of elements that displays metallic properties.

There are two types of alloys. In a **substitutional alloy,** some of the metal atoms in a crystal lattice are replaced by other atoms (usually of comparable size). Examples are brass, in which approximately one third of the atoms in a copper crystal are replaced by zinc atoms, and pewter, an alloy of tin that contains 7% copper, 6% bismuth, and 2% antimony. In an **interstitial alloy,** atoms of one or more additional elements enter the interstitial sites of the host metal lattice. An example is steel, in which carbon atoms occupy interstitial sites of an iron crystal, making the material stronger and harder than pure iron. Mild steel contains less than 0.2% C and is used for nails, whereas high-carbon steels can contain up to 1.5% C and are used in specialty applications such as tools and springs. *Alloy steels* are both substitutional and interstitial; atoms from metals such as chromium and vanadium substitute for iron atoms, with carbon remaining in interstitial sites. Alloy steels have a variety of specialized purposes, ranging from cutlery to bicycle frames.

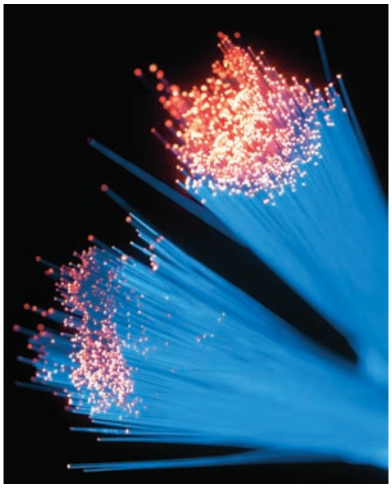

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FIGURE 21.31 Optical fibers (extremely thin glass fibers of specialized composition) carry information in the form of light waves.

Amorphous Solids and Glasses

The arrangements of atoms, ions, or molecules in crystalline solids exhibit high degrees of spatial order. Now let us briefly consider solids that lack this characteristic. **Amorphous solids,** commonly called **glasses,** resemble crystalline solids in many respects. They may have chemical compositions, mechanical properties such as hardness and elasticity, and electrical and magnetic properties that are similar to those of crystals. Like crystals, glasses may have molecular, ionic, covalent, or metallic bonding. On an atomic scale, however, amorphous solids lack the regular periodic structure of crystals. They are states of matter in which so many defects are present that crystalline order is destroyed.

Some substances have a strong tendency to solidify as glasses. The best example is the material used in common window panes, with the approximate chemical formula $Na_2O{\cdot}CaO{\cdot}(SiO_2)_6$. This is a partly ionic, partly covalent material with Na^+ and Ca^{2+} ions distributed through a covalently bonded Si—O network. Glass-forming ability is not restricted to a few special materials, however. If a substance can be liquefied, it can almost certainly be prepared in an amorphous state. Even metals, which are known primarily in the crystalline state, have been made into amorphous solids. The trick is to bypass crystallization by cooling molten material very fast. One technique involves shooting a jet of liquid metal at a rapidly rotating cold cylinder, which produces a continuous ribbon of amorphous metal at a rate up to 2 km per minute.

On the molecular level, a strong tendency to form glasses is associated with the presence of long or irregularly shaped molecules that can easily become tangled and disordered. Even slowly cooling a liquid assembly of such molecules may not afford enough time for them to organize into a crystalline lattice before solidification. Instead of a sharp liquid-to-crystal transition, such glass-formers transform continuously, over a range of temperature, into amorphous solids. They lend themselves to fabrication into articles of every conceivable shape, because the flow properties of the work piece can be managed by controlling its temperature. This plasticity is the reason that glass has played an indispensable role in science, industry, and the arts.

One of the most exciting new uses of a glass is the transmission of voice messages, television images, and data as light pulses. Tens of thousands of audio messages can be transmitted simultaneously through glass fibers no greater in diameter than a human hair. This is done by encoding the audio signal into electronic impulses that modulate light from a laser source. The light then passes down the glass fiber as though it were a tube. Chemical control of the glass composition reduces light loss and permits messages to travel many kilometers without amplification (Fig. 21.31).

CHAPTER SUMMARY

This chapter describes the distinctive properties of solids as the consequences of the collective behavior of an extended array of chemical bonds. The chemical bonds involved are already familiar in the context of isolated molecules. What is new here is the extended array of these bonds in the solid state. We can determine the array experimentally by x-ray diffraction. To describe the array we introduce the concepts of local symmetry and repetitive, long-range order; together, these define the unit cell and the crystal lattice. By placing structural elements at the points of the lattice, we complete the description of the structure of a perfect crystal. The number of atoms per unit cell depends on packing density of the atoms in the lattice. The properties of different classes of solids depend on the type of bonding involved: ionic, covalent, metallic, or molecular. The perfect crystal is the fundamental starting point for investigations in the solid state. Practical materials can be described and categorized by the nature and extent of their deviations from perfect crystal structure.

CUMULATIVE EXERCISE

Phosphorus

Solid elemental phosphorus appears in a rich variety of forms, with crystals in all seven crystal systems reported under various conditions of temperature, pressure, and sample preparation.

(a) The thermodynamically stable form of phosphorus under room conditions is black phosphorus. Its unit cell is orthorhombic with edges of lengths 3.314, 4.376, and 10.48 Å. Calculate the volume of one unit cell, and determine the number of phosphorus atoms per unit cell, if the density of this form of phosphorus is 2.69 g cm^{-3}.

(b) The form of phosphorus that is easiest to prepare from the liquid or gaseous state is white phosphorus, which consists of P_4 molecules in a cubic lattice. When x-rays of wavelength 2.29 Å are scattered from the parallel faces of its unit cells, the first-order Bragg diffraction is observed at an angle 2θ of 7.10°. Calculate the length of the unit-cell edge for white phosphorus. At what angle will third-order Bragg diffraction be seen?

(c) Amorphous red phosphorus has been reported to convert to monoclinic, triclinic, tetragonal, and cubic red forms with different heat treatments. Identify the changes in the shape of the unit cell as a cubic lattice is converted first to tetragonal, then monoclinic, then triclinic.

(d) A monoclinic form of red phosphorus has been studied that has cell edge lengths 9.21, 9.15, and 22.60 Å, with an angle β of 106.1°. Each unit cell contains 84 atoms of phosphorus. Estimate the density of this form of phosphorus.

(e) Phosphorus forms many compounds with other elements. Describe the nature of the bonding in the solids white elemental phosphorus (P_4), black elemental phosphorus, sodium phosphate (Na_3PO_4), and phosphorus trichloride (PCl_3).

Answers

(a) Volume is 152.0 Å^3; eight atoms per unit cell

(b) 18.5 Å; angle $2\theta = 21.4°$

(c) Cubic to tetragonal: One cell edge is stretched or shrunk. Tetragonal to monoclinic: A second cell edge is stretched or shrunk, and the angles between two adjacent faces (and their opposite faces) are changed from 90°. Monoclinic to triclinic: The remaining two angles between faces are deformed from 90°.

(d) 2.36 g cm^{-3}

(e) P_4(white) and PCl_3 are molecular solids; P(black) is covalent; Na_3PO_4 is ionic.


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Two forms of elemental phosphorus: white and red.

CHAPTER REVIEW

- Solids are distinguished from liquids and gases by their rigidity. Solids retain their shape and exhibit structural strength when external forces are applied. These properties originate in the strong, directional chemical bonds between the atoms in solids.
- Solids whose structures are highly ordered and symmetrical over macroscopic distances are called crystals. Concepts and methods have been developed to define and measure the structures of crystals.

Crystal structure is defined in terms of the crystal lattice, a mathematical abstraction that represents the ordered and repetitive nature of the structure. In effect the lattice is a set of coordinates for locating each atom in the structure of a network. The lattice embodies all the symmetry in the structure. Lattice points are identified by the fundamental symmetry operations of rotation, reflection, and inversion.

The unit cell is the smallest region of a crystal lattice that contains all the structural information about the crystal. So, the crystal lattice is visualized as a stack of multiple identical unit cells. Each unit cell has characteristic lengths and angles. There are seven types of crystal structures, each defined by the properties of its unit cell: hexagonal, cubic, tetragonal, trigonal, orthorhombic, monoclinic, and triclinic.

The distance d between planes in a crystal can be measured experimentally by x-ray diffraction. It is related to the wavelength λ of the radiation and the diffraction angle θ by Bragg's law $n\lambda = 2d \sin \theta$, where n is the order of the diffraction.

Once the crystal lattice has been identified, description of the structure is completed by specifying the structural elements that are located at lattice points. The resulting structures are named by characteristics of the unit cell. Three examples are displayed by the elemental metals.

Simple cubic (one atom per unit cell)	Po
Body-centered cubic (two atoms per unit cell)	alkali metals
Face-centered cubic (four atoms per unit cell)	Al, Ni, Cu, Ag

- Different types of chemical bonding appear in solids and are responsible for the differences in mechanical and structural properties of different types of solids.
- Because electrostatic forces are strong and operate over large distances, ionic crystals are hard, brittle solids that have high melting points and are poor conductors of heat and electricity They crystallize in structures determined primarily by atomic packing density.
  zinc blende structure for cation-anion radius ratio smaller than 0.414
  rock-salt structure for cation-anion radius ratio between 0.414 and 0.732
  cesium chloride structure for cation-anion radius ratio greater than 0.732
- Bonding in metallic crystals is explained as a sea of delocalized electrons around positively charged ions located at the lattice sites. The number density of electrons is equal to the number density of positive ions, so the metal is electrically neutral. The bonds are quite strong, evidenced by the high boiling points of metals. Metals are malleable and ductile because the highly mobile electrons can rapidly adjust when lattice ions are pushed to new locations by external mechanical forces. Metals are good conductors of heat and electricity because the delocalized electrons respond easily to applied external fields.
- Covalent crystals are held together by strong, highly directional bonds usually described by the valence bond hybrid orbital method. Each atom is part of a large extended single molecule that is the crystal itself. Because of the nature of their bonds, covalent crystals have very high melting points and are hard and brittle.
- Molecular crystals are held together by van der Waals forces, the same as the intermolecular forces in gases and liquids. Because these are much weaker than ionic, metallic, and covalent bonds, the molecular crystals are usually soft, easily deformed, and have low melting points.

- Real-world crystals do not have perfect symmetry and order. It is useful to characterize practical materials by the ways in which they deviate from the structure of the perfect crystal models described earlier.

  Point defects where atoms are missing from lattice sites are called vacancies, or Schottky defects. Their number density depends on the temperature and on the Gibbs free energy of formation of defects.

  Point defects where atoms are located between lattice sites are called interstitials. If a lattice atom is displaced to an interstitial site, the combination of the defect and the interstitial is called a Frenkel defect.
- Diffusion in solids occurs as Schottky or Frenkel defects hop from one lattice site to another by a thermally activated process akin to chemical reactions.
- Amorphous solids, or glasses, may have chemical compositions and mechanical properties similar to crystalline materials, and they may have ionic, metallic, covalent, or molecular bonding. But at the microscopic level they lack crystalline order. This arises from kinetic effects during solidification that reduce the mobility of atoms or molecules and prevent them from achieving ordered structures. Long or irregularly shaped molecules that are easily entangled lead to glass formation.

CONCEPTS & SKILLS

After studying this chapter and working the problems that follow, you should be able to:

1. Identify the symmetry elements of different crystal systems (Section 21.1, Problems 1–4).
2. Explain how x-rays and neutrons are diffracted by crystals, and use information from such experiments to calculate lattice spacings (Section 21.1, Problems 5–10).
3. Describe the packing of atoms in simple crystal lattices (Section 21.2, Problems 11–24).
4. Compare the natures of the forces that hold atoms or molecules in their lattice sites in ionic, metallic, covalent, and molecular crystals (Section 21.3, Problems 27–32).
5. Calculate lattice energies of molecular and ionic crystals (Section 21.4, Problems 35–38).
6. Describe the kinds of equilibrium defects that are present in crystalline solids and the properties of amorphous solids (Section 21.5).
7. Determine the oxidation states present in nonstoichiometric solids (Section 21.5, Problems 41–42).

KEY EQUATIONS

$$n\lambda = 2d\sin\theta \qquad n = 1, 2, 3, \ldots \qquad \textbf{(Section 21.1)}$$

$$V_c = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma} \qquad \textbf{(Section 21.2)}$$

$$\text{lattice energy} = \frac{N_A e^2}{4\pi\epsilon_0 R_0} M \qquad \textbf{(Section 21.4)}$$

$$D = D_0 \exp[-E_a/RT] \qquad \textbf{(Section 21.5)}$$

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G. Problems that are more challenging are indicated with asterisks.

Crystal Symmetry and the Unit Cell

1. Which of the following has 3-fold rotational symmetry? Explain.
   (a) An isosceles triangle
   (b) An equilateral triangle
   (c) A tetrahedron
   (d) A cube

2. Which of the following has 4-fold rotational symmetry? Explain.
   (a) A cereal box (exclusive of the writing on the sides)
   (b) A stop sign (not counting the writing)
   (c) A tetrahedron
   (d) A cube

3. Identify the symmetry elements of the CCl_2F_2 molecule (see Fig. 12.15).

4. Identify the symmetry elements of the PF_5 molecule (see Fig. 3.20a).

5. The second-order Bragg diffraction of x-rays with $\lambda = 1.660$ Å from a set of parallel planes in copper occurs at an angle $2\theta = 54.70°$. Calculate the distance between the scattering planes in the crystal.

6. The second-order Bragg diffraction of x-rays with $\lambda = 1.237$ Å from a set of parallel planes in aluminum occurs at an angle $2\theta = 35.58°$. Calculate the distance between the scattering planes in the crystal.

7. The distance between members of a set of equally spaced planes of atoms in crystalline lead is 4.950 Å. If x-rays with $\lambda = 1.936$ Å are diffracted by this set of parallel planes, calculate the angle 2θ at which fourth-order Bragg diffraction will be observed.

8. The distance between members of a set of equally spaced planes of atoms in crystalline sodium is 4.28 Å. If x-rays with $\lambda = 1.539$ Å are diffracted by this set of parallel planes, calculate the angle 2θ at which second-order Bragg diffraction will be observed.

9. The members of a series of equally spaced parallel planes of ions in crystalline LiCl are separated by 2.570 Å. Calculate all the angles 2θ at which diffracted beams of various orders may be seen, if the x-ray wavelength used is 2.167 Å.

10. The members of a series of equally spaced parallel planes in crystalline vitamin B_{12} are separated by 16.02 Å. Calculate all the angles 2θ at which diffracted beams of various orders may be seen, if the x-ray wavelength used is 2.294 Å.

Crystal Structure

11. A crucial protein at the photosynthetic reaction center of the purple bacterium *Rhodopseudomonas viridis* (see Section 20.6) has been separated from the organism, crystallized, and studied by x-ray diffraction. This substance crystallizes with a primitive unit cell in the tetragonal system. The cell dimensions are $a = b = 223.5$ Å and $c = 113.6$ Å.
   (a) Determine the volume, in cubic angstroms, of this cell.
   (b) One of the crystals in this experiment was box-shaped, with dimensions 1 × 1 × 3 mm. Compute the number of unit cells in this crystal.

12. Compute the volume (in cubic angstroms) of the unit cell of potassium hexacyanoferrate(III) ($K_3Fe(CN)_6$), a substance that crystallizes in the monoclinic system with $a = 8.40$ Å, $b = 10.44$ Å, and $c = 7.04$ Å and with $\beta = 107.5°$.

13. The compound $Pb_4In_3B_{17}S_{18}$ crystallizes in the monoclinic system with a unit cell having $a = 21.021$ Å, $b = 4.014$ Å, $c = 18.898$ Å, and the only non-90° angle equal to 97.07°. There are two molecules in every unit cell. Compute the density of this substance.

14. Strontium chloride hexahydrate ($SrCl_2{\cdot}6H_2O$) crystallizes in the trigonal system in a unit cell with $a = 8.9649$ Å and $\alpha = 100.576°$. The unit cell contains three formula units. Compute the density of this substance.

15. At room temperature, the edge length of the cubic unit cell in elemental silicon is 5.431 Å, and the density of silicon at the same temperature is 2.328 g cm^{-3}. Each cubic unit cell contains eight silicon atoms. Using only these facts, perform the following operations.
   (a) Calculate the volume (in cubic centimeters) of one unit cell.
   (b) Calculate the mass (in grams) of silicon present in a unit cell.
   (c) Calculate the mass (in grams) of an atom of silicon.
   (d) The mass of an atom of silicon is 28.0855 u. Estimate Avogadro's number to four significant figures.

16. One form of crystalline iron has a bcc lattice with an iron atom at every lattice point. Its density at 25°C is 7.86 g cm^{-3}. The length of the edge of the cubic unit cell is 2.87 Å. Use these facts to estimate Avogadro's number.

17. Sodium sulfate (Na_2SO_4) crystallizes in the orthorhombic system in a unit cell with $a = 5.863$ Å, $b = 12.304$ Å, and $c = 9.821$ Å. The density of these crystals is 2.663 g cm^{-3}. Determine how many Na_2SO_4 formula units are present in the unit cell.

18. The density of turquoise, $CuAl_6(PO_4)_4(OH)_8(H_2O)_4$, is 2.927 g cm^{-3}. This gemstone crystallizes in the triclinic system with cell constants $a = 7.424$ Å, $b = 7.629$ Å, $c = 9.910$ Å, $\alpha = 68.61°$, $\beta = 69.71°$, and $\gamma = 65.08°$. Calculate the volume of the unit cell, and determine how many copper atoms are present in each unit cell of turquoise.

19. An oxide of rhenium has a structure with a Re atom at each corner of the cubic unit cell and an O atom at the center of each edge of the cell. What is the chemical formula of this compound?

20. The mineral perovskite has a calcium atom at each corner of the unit cell, a titanium atom at the center of the unit cell, and an oxygen atom at the center of each face. What is the chemical formula of this compound?

* **21.** Iron has a body-centered cubic structure with a density of 7.86 g cm^{-3}.
(a) Calculate the nearest neighbor distance in crystalline iron.
(b) What is the lattice parameter for the cubic unit cell of iron?
(c) What is the atomic radius of iron?

22. The structure of aluminum is fcc and its density is $\rho = 2.70$ g cm^{-3}.
(a) How many Al atoms belong to a unit cell?
(b) Calculate a, the lattice parameter, and d, the nearest neighbor distance.

23. Sodium has the body-centered cubic structure, and its lattice parameter is 4.28 Å.
(a) How many Na atoms does a unit cell contain?
(b) What fraction of the volume of the unit cell is occupied by Na atoms, if they are represented by spheres in contact with one another?

24. Nickel has a fcc structure with a density of 8.90 g cm^{-3}.
(a) Calculate the nearest neighbor distance in crystalline nickel.
(b) What is the atomic radius of nickel?
(c) What is the radius of the largest atom that could fit into the interstices of a nickel lattice, approximating the atoms as spheres?

25. Calculate the ratio of the maximum radius of an interstitial atom at the center of a simple cubic unit cell to the radius of the host atom.

26. Calculate the ratio of the maximum radius of an interstitial atom at the center of each face of a bcc unit cell to the radius of the host atom.

Cohesion in Solids

27. Classify each of the following solids as molecular, ionic, metallic, or covalent.
(a) $BaCl_2$ (b) SiC
(c) CO (d) Co

28. Classify each of the following solids as molecular, ionic, metallic, or covalent.
(a) Rb (b) C_5H_{12}
(c) B (d) Na_2HPO_4

29. The melting point of cobalt is 1495°C, and that of barium chloride is 963°C. Rank the four substances in problem 27 from lowest to highest in melting point.

30. The boiling point of pentane (C_5H_{12}) is slightly less than the melting point of rubidium. Rank the four substances in problem 28 from lowest to highest in melting point.

31. Explain the relationship between the number of bonds that can be formed by a typical atom in a crystal and the possibility of forming linear, two-dimensional, and three-dimensional network structures.

32. Although large crystals of sugar (rock candy) and large crystals of salt (rock salt) have different geometric shapes, they look much the same to the untrained observer. What physical tests other than taste might be performed to distinguish between these two crystalline substances?

33. By examining Figure 21.17, determine the number of nearest neighbors, second nearest neighbors, and third nearest neighbors of a Cs^+ ion in crystalline CsCl. The nearest neighbors of the Cs^+ ion are Cl^- ions, and the second nearest neighbors are Cs^+ ions.

34. Repeat the determinations of the preceding problem for the NaCl crystal, referring to Figure 21.16.

A DEEPER LOOK *Lattice Energies of Crystals*

35. Calculate the energy needed to dissociate 1.00 mol of crystalline RbCl into its gaseous ions if the Madelung constant for its structure is 1.7476 and the radii of Rb^+ and Cl^- are 1.48 Å and 1.81 Å, respectively. Assume that the repulsive energy reduces the lattice energy by 10% from the pure Coulomb energy.

36. Repeat the calculation of problem 35 for CsCl, taking the Madelung constant from Table 21.5 and taking the radii of Cs^+ and Cl^- to be 1.67 Å and 1.81 Å.

37. (a) Use the Born–Haber cycle, with data from Appendices D and F, to calculate the lattice energy of LiF.
(b) Compare the result of part (a) with the Coulomb energy calculated by using an Li—F separation of 2.014 Å in the LiF crystal, which has the rock-salt structure.

38. Repeat the calculations of problem 37 for crystalline KBr, which has the rock-salt structure with a K—Br separation of 3.298 Å.

Defects and Amorphous Solids

39. Will the presence of Frenkel defects change the measured density of a crystal?

40. What effect will the (unavoidable) presence of Schottky defects have on the determination of Avogadro's number via the method described in problems 15 and 16?

41. Iron(II) oxide is nonstoichiometric. A particular sample was found to contain 76.55% iron and 23.45% oxygen by mass.
(a) Calculate the empirical formula of the compound (four significant figures).
(b) What percentage of the iron in this sample is in the +3 oxidation state?

42. A sample of nickel oxide contains 78.23% Ni by mass.
(a) What is the empirical formula of the nickel oxide to four significant figures?
(b) What fraction of the nickel in this sample is in the +3 oxidation state?

ADDITIONAL PROBLEMS

43. Some water waves with a wavelength of 3.0 m are diffracted by an array of evenly spaced posts in the water. If the rows of posts are separated by 5.0 m, calculate the angle 2θ at which the first-order "Bragg diffraction" of these water waves will be seen.

44. A crystal scatters x-rays of wavelength $\lambda = 1.54$ Å at an angle 2θ of 32.15°. Calculate the wavelength of the x-rays in another experiment if this same diffracted beam from the same crystal is observed at an angle 2θ of 34.46°.

45. The number of beams diffracted by a single crystal depends on the wavelength λ of the x-rays used and on the volume associated with one lattice point in the crystal—that is, on the volume V_p of a primitive unit cell. An approximate formula is

$$\text{number of diffracted beams} = \frac{4}{3}\pi\left(\frac{2}{\lambda}\right)^3 V_p$$

(a) Compute the volume of the conventional unit cell of crystalline sodium chloride. This cell is cubic and has an edge length of 5.6402 Å.

(b) The NaCl unit cell contains four lattice points. Compute the volume of a primitive unit cell for NaCl.

(c) Use the formula given in this problem to estimate the number of diffracted rays that will be observed if NaCl is irradiated with x-rays of wavelength 2.2896 Å.

(d) Use the formula to estimate the number of diffracted rays that will be observed if NaCl is irradiated with x-rays having the shorter wavelength 0.7093 Å.

46. If the wavelength λ of the x-rays is too large relative to the spacing of planes in the crystal, no Bragg diffraction will be seen because $\sin\theta$ would be larger than 1 in the Bragg equation, even for $n = 1$. Calculate the longest wavelength of x-rays that can give Bragg diffraction from a set of planes separated by 4.20 Å.

47. The crystal structure of diamond is fcc, and the atom coordinates in the unit cell are $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \mathrm{v})$, $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, $(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$, $(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$, and $(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$. The lattice parameter is $a = 3.57$ Å. What is the C—C bond distance in diamond?

48. Polonium is the only element known to crystallize in the simple cubic lattice.

(a) What is the distance between nearest neighbor polonium atoms if the first-order diffraction of x-rays with $\lambda = 1.785$ Å from the parallel faces of its unit cells appears at an angle of $2\theta = 30.96°$ from these planes?

(b) What is the density of polonium in this crystal (in g $\mathrm{cm^{-3}}$)?

49. At room temperature, monoclinic sulfur has the unit-cell dimensions $a = 11.04$ Å, $b = 10.98$ Å, $c = 10.92$ Å, and $\beta = 96.73°$. Each cell contains 48 atoms of sulfur.

(a) Explain why it is not necessary to give the values of the angles α and γ in this cell.

(b) Compute the density of monoclinic sulfur (in g $\mathrm{cm^{-3}}$).

50. A compound contains three elements: sodium, oxygen, and chlorine. It crystallizes in a cubic lattice. The oxygen atoms are at the corners of the unit cells, the chlorine atoms are at the centers of the unit cells, and the sodium atoms are at the centers of the faces of the unit cells. What is the formula of the compound?

***51.** Show that the radius of the largest sphere that can be placed in a tetrahedral interstitial site in an fcc lattice is $0.225r_1$, where r_1 is the radius of the atoms making up the lattice. (*Hint:* Consider a cube with the centers of four spheres placed at alternate corners, and visualize the tetrahedral site at the center of the cube. What is the relationship between r_1 and the length of a diagonal of a face? The length of a body diagonal?)

52. What is the closest packing arrangement possible for a set of thin circular discs lying in a plane? What fraction of the area of the plane is occupied by the discs? Show how the same reasoning can be applied to the packing of infinitely long, straight cylindrical fibers.

53. Name two elements that form molecular crystals, two that form metallic crystals, and two that form covalent crystals. What generalizations can you make about the portions of the periodic table where each type is found?

54. The nearest-neighbor distance in crystalline LiCl (rock-salt structure) is 2.570 Å; the bond length in a gaseous LiCl molecule is significantly shorter, 2.027 Å. Explain.

55. **(a)** Using the data of Table 9.4, estimate the lattice energy and intermolecular separation of nitrogen in its solid state, assuming an fcc structure for the solid lattice.

(b) The density of cubic nitrogen is 1.026 g $\mathrm{cm^{-3}}$. Calculate the lattice parameter a and the nearest neighbor distance. Compare your answer with that from part (a).

***56.** Solid $\mathrm{CuI_2}$ is unstable relative to CuI at room temperature, but $\mathrm{CuBr_2}$, $\mathrm{CuCl_2}$, and $\mathrm{CuF_2}$ are all stable relative to the copper(I) halides. Explain by considering the steps in the Born–Haber cycle for these compounds.

57. A crystal of sodium chloride has a density of 2.165 g $\mathrm{cm^{-3}}$ in the absence of defects. Suppose a crystal of NaCl is grown in which 0.15% of the sodium ions and 0.15% of the chloride ions are missing. What is the density in this case?

58. The activation energy for the diffusion of sodium atoms in the crystalline state is 42.22 kJ $\mathrm{mol^{-1}}$, and $D_0 = 0.145\ \mathrm{cm^2\ s^{-1}}$.

(a) Calculate the diffusion constant $D = D_0 \exp(-E_a/RT)$ of sodium in the solid at its melting point (97.8°C).

(b) What is the root-mean-square displacement of an average sodium atom from an arbitrary origin after the lapse of 1.0 hour at $t = 97.8°\mathrm{C}$? (*Hint:* Use Equation 9.37 in Chapter 9.)

59. A compound of titanium and oxygen contains 28.31% oxygen by mass.

(a) If the compound's empirical formula is $\mathrm{Ti}_x\mathrm{O}$, calculate x to four significant figures.

(b) The nonstoichiometric compounds $\mathrm{Ti}_x\mathrm{O}$ can be described as having a $\mathrm{Ti^{2+}}$—$\mathrm{O^{2-}}$ lattice in which certain $\mathrm{Ti^{2+}}$ ions are missing or are replaced by $\mathrm{Ti^{3+}}$ ions. Calculate the fraction of $\mathrm{Ti^{2+}}$ sites in the nonstoichiometric compound that are vacant and the fraction that are occupied by $\mathrm{Ti^{3+}}$ ions.

60. Classify the bonding in the following amorphous solids as molecular, ionic, metallic, or covalent.

(a) Amorphous silicon, used in photocells to collect light energy from the sun

(b) Polyvinyl chloride, a plastic of long-chain molecules composed of $-\mathrm{CH_2CHCl}-$ repeating units, used in pipes and siding

(c) Soda-lime-silica glass, used in windows

(d) Copper-zirconium glass, an alloy of the two elements with approximate formula $\mathrm{Cu_3Zr_2}$, used for its high strength and good conductivity

CUMULATIVE PROBLEMS

61. Sodium hydride (NaH) crystallizes in the rock-salt structure, with four formula units of NaH per cubic unit cell. A beam of monoenergetic neutrons, selected to have a velocity of 2.639×10^3 m s^{-1}, is scattered in second order through an angle of $2\theta = 36.26°$ by the parallel faces of the unit cells of a sodium hydride crystal.
    - (a) Calculate the wavelength of the neutrons.
    - (b) Calculate the edge length of the cubic unit cell.
    - (c) Calculate the distance from the center of an Na^+ ion to the center of a neighboring H^- ion.
    - (d) If the radius of a Na^+ ion is 0.98 Å, what is the radius of an H^- ion, assuming the two ions are in contact?

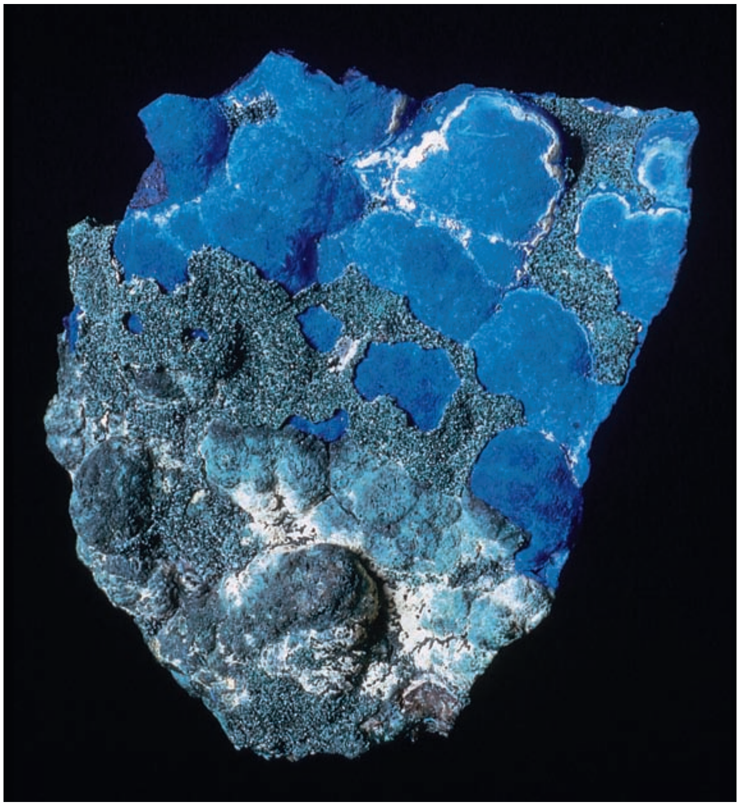
62. Chromium(III) oxide has a structure in which chromium ions occupy two thirds of the octahedral interstitial sites in a hexagonal close-packed lattice of oxygen ions. What is the *d*-electron configuration on the chromium ion?

63. A useful rule of thumb is that in crystalline compounds every nonhydrogen atom occupies 18 Å^3, and the volume occupied by hydrogen atoms can be neglected. Using this rule, estimate the density of ice (in g cm^{-3}). Explain why the answer is so different from the observed density of ice.

64. Estimate, for the F-centers in CaF_2, the wavelength of maximum absorption in the visible region of the spectrum that will give rise to the color shown in Figure 21.30.

CHAPTER 22

Inorganic Materials



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Azurite is a basic copper carbonate with chemical formula $Cu_3(CO_3)_2(OH)_2$.

Having laid the conceptual foundation for relating properties of solids to chemical bonding in Chapter 21, we turn now to applications of these concepts to three important classes of materials: ceramics, electronic materials, and optical materials. All of these are synthetic materials fashioned from inorganic, nonmetallic substances by chemical methods of synthesis and processing.

Ceramics are one of the oldest classes of materials prepared by humankind. New discoveries in ceramics are occurring at a startling rate, and major new technologic advances will certainly come from these discoveries. Ceramics have value both as structural materials—the role emphasized in this chapter—and for their wide range of electronic and optical properties.

High-speed computing, fast communication, and rapid display of information were major technologic achievements in the second half of the 20th century. These developments will grow even more rapidly in the 21st century, when every home will be digitally connected to the Internet and every cell phone will display images requiring broadband transmission. These developments were made possible by the "microelectronics revolution," beginning with the first integrated circuits fabricated on microchips by Jack Kilby at Texas Instruments and Robert Noyce at Fairchild in 1958 to 1959.[1] The speed of computers increased dramatically through advances in transistor design; advances in the solid-state laser enabled high-speed communication via fiber optics. All these advances in device design relied critically on equally dramatic accomplishments in the growth and processing of materials, which in every case involved making and breaking chemical bonds in solid-state materials. Our goals in this chapter are to introduce the optical and electronic properties of materials and to show how they depend on chemical structure.

Electronic properties describe the movement of charged particles in a material in response to an applied electric field. If the charges are free to move throughout the material, the process is *electrical conduction,* measured by the *electrical conductivity* of the material. Differences in the magnitude of the conductivity distinguish metals, semiconductors, and insulators. If the charges can move only limited distances and are then halted by opposing binding forces, separation of positive and negative charges leads to *electric polarization* of the material, measured by its *dielectric constant.* Conduction involves dissipation of energy as heat, whereas polarization involves storage of potential energy in the material.

Optical properties describe the response of a material to electromagnetic radiation, particularly visible light. The list of optical properties is long, including reflection of light from a surface, refraction (bending the direction) of light as it passes from one medium into another, absorption, and transmission. We limit the discussion here to the generation and detection of light in solid materials, as extensions of the molecular processes of emission and excitation already described in Chapter 20. The absorption of light creates the bright colors of inorganic pigments and the conversion of solar energy into electrical energy in solar cells.

In this survey of mechanical, electrical, and optical properties, keep two questions in mind: (1) How does a material respond on an atomic level to applied mechanical stress and to electrical and optical fields? (2) If the chemical structure is modified, how does this change influence the response of the material to these forces?

22.1 Minerals: Naturally Occurring Inorganic Materials

This chapter begins with a survey of the naturally occurring inorganic, nonmetallic minerals that are the starting materials for synthesis and processing of inorganic materials.

Silicates

Silicon and oxygen make up most of the earth's crust, with oxygen accounting for 47% and silicon for 28% of its mass. The silicon–oxygen bond is strong and partially ionic. It forms the basis for a class of minerals called **silicates,** which make up the bulk of the rocks, clays, sand, and soils in the earth's crust. From time immemorial, silicates have provided the ingredients for building materials such as bricks, cement, concrete, and glass (which are considered later in this chapter).

The structure-building properties of silicates (Table 22.1) originate in the tetrahedral orthosilicate anion (SiO_4^{4-}), in which the negative charge of the silicate ion

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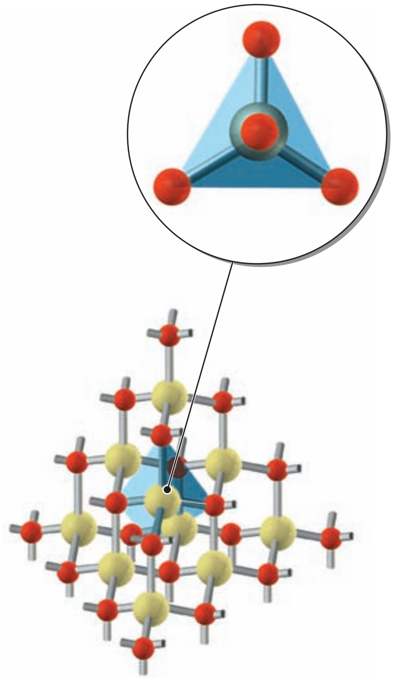
[1] Kilby was awarded the Nobel Prize in Physics in 2000, but Noyce, who had died, did not share the award. The Nobel Prize is not awarded posthumously.



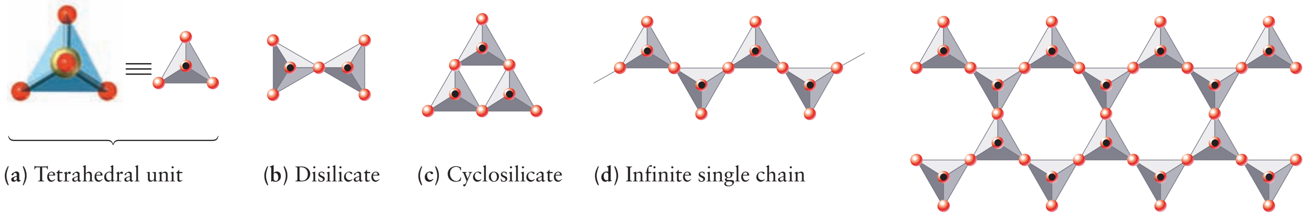
Each SiO_2 unit shares O—Si—O bonds with other SiO_2 units arranged in a lattice of tetrahedra. Si atoms are shown in yellow and O atoms in red.

is balanced by the compensating charge of one or more cations. The simplest silicates consist of individual SiO_4^{4-} anions (Fig. 22.1a), with cations arranged around them on a regular crystalline lattice. Such silicates are properly called **orthosilicates.** Examples are forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4), which are the extreme members of a class of minerals called **olivines,** $[Mg,Fe]_2SiO_4$. There is a continuous range of proportions of magnesium and iron in the olivines.

Other silicate structures form when two or more SiO_4^{4-} tetrahedra link and share oxygen vertices. The simplest such minerals are the **disilicates,** such as thortveitite, $Sc_2(Si_2O_7)$, in which two tetrahedra are linked (see Fig. 22.1b). Additional linkages of tetrahedra create the ring, chain, sheet, and network structures shown in Figure 22.1 and listed in Table 22.1. In each of these, the fundamental tetrahedron is readily identified, but the Si : O ratio is no longer 4 because oxygen (O) atoms are shared at the linkages.

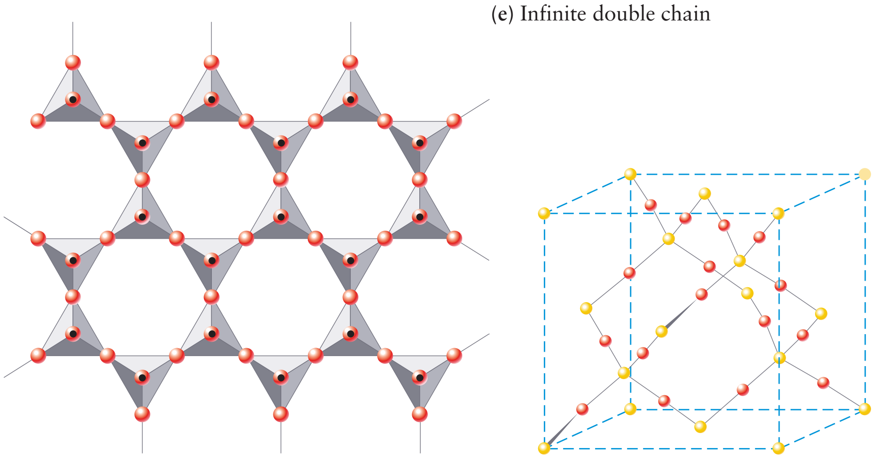
TABLE 22.1 **Silicate Structures**

Structure	Figure Number	Corners Shared at Each Si atom	Repeat Unit	Si : O Ratio	Example
Tetrahedra	22.1a	0	SiO_4^{4-}	1 : 4	Olivines
Pairs of tetrahedra	22.1b	1	$Si_2O_7^{6-}$	$1:3\frac{1}{2}$	Thortveitite
Closed rings	22.1c	2	SiO_3^{2-}	1 : 3	Beryl
Infinite single chains	22.1d	2	SiO_3^{2-}	1 : 3	Pyroxenes
Infinite double chains	22.1e	$2\frac{1}{2}$	$Si_4O_{11}^{6-}$	$1:2\frac{3}{4}$	Amphiboles
Infinite sheets	22.1f	3	$Si_2O_5^{2-}$	$1:2\frac{1}{2}$	Talc
Infinite network	22.1g	4	SiO_2	1 : 2	Quartz



(a) Tetrahedral unit (b) Disilicate (c) Cyclosilicate (d) Infinite single chain

(e) Infinite double chain



(f) Infinite sheet (g) Infinite network (cristobalite, SiO_2)

FIGURE 22.1 Classes of silicate structures. (a) Symbol used for the SiO_4^{4-} tetrahedron. This top view of the symbol shows a red circle to represent the fourth oxygen atom at the top of the tetrahedron. The black dot represents the silicon atom at the center of the tetrahedron. Bear in mind that all of these structures are actually three dimensional. Planar projections are used here for convenience of representation. (b) Disilicate. (c) Cyclosilicate. (d) Infinite single chain. (e) Infinite double chain. (f) Infinite sheet. (g) Infinite network (cristobalite, SiO_2).


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FIGURE 22.2 The mineral quartz is one form of silica, SiO_2.

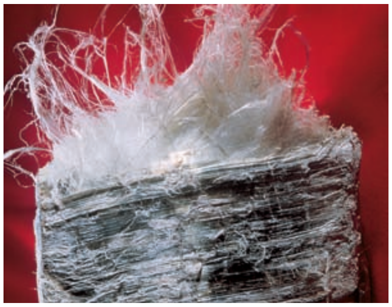
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FIGURE 22.3 The fibrous structure of asbestos is apparent in this sample.

EXAMPLE 22.1

By referring to Table 22.1, predict the structural class in which the mineral Egyptian blue ($CaCuSi_4O_{10}$) belongs. Give the oxidation state of each of its atoms.

SOLUTION

Because the silicon/oxygen (Si:O) ratio is 4:10, or $1:2\frac{1}{2}$, this mineral should have an infinite sheet structure with the repeating unit $Si_2O_5^{2-}$. The oxidation states of Si and O are +4 and −2, as usual, and that of calcium (Ca) is +2. For the total oxidation number per formula unit to sum to 0, the oxidation state of copper (Cu) must be +2.

Related Problems: 3, 4

The physical properties of the silicates correlate closely with their structures. Talc, $Mg_3(Si_4O_{10})(OH)_2$, is an example of an infinite layered structure (see Fig. 22.1f). In talc, all of the bonding interactions among the atoms occur in a single layer. Layers of talc sheets are attracted to one another only by van der Waals interactions, which (being weak) permit one layer to slip easily across another. This accounts for the slippery feel of talc (called talcum powder). When all four vertices of each tetrahedron are linked to other tetrahedra, three-dimensional network structures such as cristobalite (see Fig. 22.1g) or quartz (Fig. 22.2) result. Note that the quartz network carries no charge; consequently, there are no cations in its structure. Three-dimensional network silicates such as quartz are much stiffer and harder than the linear and layered silicates, and they resist deformation well.

Asbestos is a generic term for a group of naturally occurring, hydrated silicates that can be processed mechanically into long fibers (Fig. 22.3). Some of these silicates, such as tremolite, $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$, show the infinite double-chain structure of Figure 22.1e. Another kind of asbestos mineral is chrysotile, $Mg_3(Si_2O_5)(OH)_4$. As the formula indicates, this mineral has a sheet structure (see Fig. 22.1f), but the sheets are rolled into long tubes. Asbestos minerals are fibrous because the bonds along the strandlike tubes are stronger than those that hold different tubes together. Asbestos is an excellent thermal insulator that does not burn, resists acids, and is strong. For many years, it was used in cement for pipes and ducts and woven into fabric to make fire-resistant roofing paper and floor tiles. Its use has decreased significantly in recent years because inhalation of its small fibers can cause the lung disease asbestosis. The risk comes with breathing asbestos dust that is raised during mining and manufacturing processes or that is released in buildings in which asbestos-containing materials are fraying, crumbling, or being removed.

Aluminosilicates

An important class of minerals called **aluminosilicates** results from the replacement of some of the Si atoms in silicates with aluminum (Al) atoms. Aluminum is the third most abundant element in the earth's crust (8% by mass), where it occurs largely in the form of aluminosilicates. Aluminum in minerals can be a simple cation (Al^{3+}), or it can replace silicon in tetrahedral coordination. When it replaces silicon, it contributes only three electrons to the bonding framework in place of the four electrons of Si atoms. The additional required electron is supplied by the ionization of a metal atom such as sodium (Na) or potassium (K); the resulting alkali-metal ions occupy nearby sites in the aluminosilicate structure.

The most abundant and important of the aluminosilicate minerals in the earth's surface are the **feldspars,** which result from the substitution of aluminum for silicon in three-dimensional silicate networks such as quartz. The Al ions must be accompanied by other cations such as sodium, potassium, or calcium to maintain overall charge neutrality. Albite is a feldspar with the chemical formula $NaAlSi_3O_8$.

In the high-temperature form of this mineral, the Al and Si atoms are distributed at random (in 1 : 3 proportion) over the tetrahedral sites available to them. At lower temperatures, other crystal structures become thermodynamically stable, with partial ordering of the Al and Si sites.

If one of the four Si atoms in the structural unit of talc, $Mg_3(Si_4O_{10})(OH)_2$, is replaced by an Al atom and a K atom is furnished to supply the fourth electron needed for bonding in the tetrahedral silicate framework, the result is the composition $KMg_3(AlSi_3O_{10})(OH)_2$, which belongs to the family of **micas** (Fig. 22.4). Mica is harder than talc, and its layers slide less readily over one another, although the crystals still cleave easily into sheets. The cations occupy sites between the infinite sheets, and the van der Waals bonding that holds adjacent sheets together in talc is augmented by an ionic contribution. The further replacement of the three Mg^{2+} ions in $KMg_3(AlSi_3O_{10})(OH)_2$ with two Al^{3+} ions gives the mineral muscovite, $KAl_2(AlSi_3O_{10})(OH)_2$. Writing its formula in this way indicates that there are Al atoms in two kinds of sites in the structure: One Al atom per formula unit occupies a tetrahedral site, substituting for one Si atom, and the other two Al atoms are between the two adjacent layers. The formulas that mineralogists and crystallographers use convey more information than the usual empirical chemical formula of a compound.


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FIGURE 22.4 Naturally occurring muscovite mica. The mechanical properties of crystals of mica are quite anisotropic. Thin sheets can be peeled off a crystal of mica by hand, but the sheets resist stresses in other directions more strongly. Transparent, thin sheets of mica, sometimes called isinglass, have been used for heat-resistant windows in stoves or in place of window glass.

Clay Minerals

Clays are minerals produced by the weathering action of water and heat on primary minerals. Their compositions can vary widely as a result of the replacement of one element with another. Invariably, they are microcrystalline or powdered in form and are usually hydrated. Often, they are used as supports for catalysts, as fillers in paint, and as ion-exchange vehicles. The clays that readily absorb water and swell are used as lubricants and bore-hole sealers in the drilling of oil wells.

The derivation of clays from talcs and micas provides a direct way to understand the structures of the clays. The infinite-sheet mica pyrophyllite, $Al_2(Si_4O_{10})(OH)_2$, serves as an example. If one of six Al^{3+} ions in the pyrophyllite structure is replaced by one Mg^{2+} ion and one Na^+ ion (which together carry the same charge), a type of clay called montmorillonite, $MgNaAl_5(Si_4O_{10})_3(OH)_6$, results. This clay readily absorbs water, which infiltrates between the infinite sheets and hydrates the Mg^{2+} and Na^+ ions there, causing the montmorillonite to swell (Fig. 22.5).

A different clay derives from the layered mineral talc, $Mg_3(Si_4O_{10})(OH)_2$. If iron(II) and aluminum replace magnesium and silicon in varying proportions and water molecules are allowed to take up positions between the layers, the swelling clay vermiculite results. When heated, vermiculite pops like popcorn, as the steam generated by the vaporization of water between the layers puffs the flakes up into a light, fluffy material with air inclusions. Because of its porous structure, vermiculite is used for thermal insulation or as an additive to loosen soils.

Zeolites

Zeolites are a class of three-dimensional aluminosilicates. Like the feldspars, they carry a negative charge on the aluminosilicate framework that is compensated by neighboring alkali-metal or alkaline-earth cations. Zeolites differ from feldspars in having much more open structures that consist of polyhedral cavities connected by tunnels (Fig. 22.6). Many zeolites are found in nature, but they can also be synthesized under conditions controlled to favor cavities of uniform size and shape. Most zeolites accommodate water molecules in their cavities, where they provide a mobile phase for the migration of the charge-compensating cations. This enables zeolites to serve as ion-exchange materials (in which one kind of positive ion can be readily exchanged for another) and is the key to their ability to soften water. Water "hardness" arises from soluble calcium and magnesium salts such as

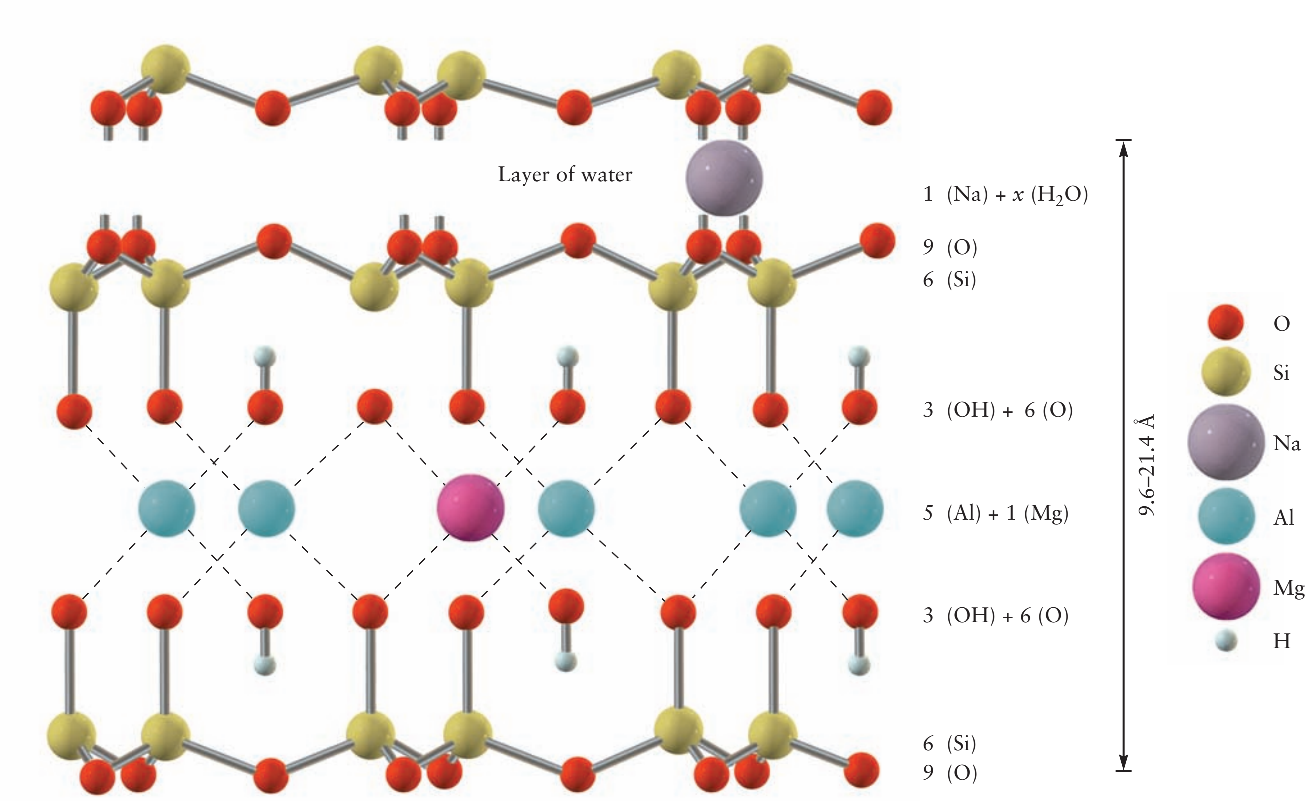

FIGURE 22.5 Structure of the clay mineral montmorillonite. Insertion of variable amounts of water causes the distance between layers to swell from 9.6 Å to more than 20 Å. When 1 Al^{3+} ion is replaced by an Mg^{2+} ion, an additional ion such as Na^+ is introduced into the water layers to maintain overall charge neutrality.

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$Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. Such salts are converted to insoluble carbonates (boiler scale) when the water is heated and form objectionable precipitates (bathtub ring) with soaps. When hard water is passed through a column packed with a zeolite that has Na ions in its structure, the Ca and Mg ions exchange with the Na ions and are removed from the water phase:

$$2\ NaZ(s) + Ca^{2+}(aq) \rightleftharpoons CaZ_2(s) + 2\ Na^+(aq)$$

When the ion-exchange capacity of the zeolite is exhausted, this reaction can be reversed by passing a concentrated solution of sodium chloride through the zeolite to regenerate it in the sodium form.

A second use of zeolites derives from the ease with which they adsorb small molecules. Their spongelike affinity for water makes them useful as drying agents; they are put between the panes of double-pane glass windows to prevent moisture from condensing on the inner surfaces. The pore size of zeolites can be selected to allow molecules that are smaller than a certain size to pass through but hold back larger molecules. Such zeolites serve as “molecular sieves”; they have been used to capture nitrogen molecules in a gas stream while permitting oxygen molecules to pass through.

Perhaps the most exciting use of zeolites is as catalysts. Molecules of varying sizes and shapes have different rates of diffusion through a zeolite; this feature enables chemists to enhance the rates and yields of desired reactions and suppress unwanted reactions. The most extensive applications of zeolites currently are in the catalytic cracking of crude oil, a process that involves breaking down long-chain hydrocarbons and re-forming them into branched-chain molecules of lower molecular mass for use in high-octane unleaded gasoline. A relatively new process uses “shape-selective” zeolite catalysts to convert methanol (CH_3OH) to high-quality gasoline. Plants have been built to make gasoline by this process, using methanol derived from coal or from natural gas.

22.2 Properties of Ceramics

The term ***ceramics*** covers synthetic materials that have as their essential components inorganic, nonmetallic materials. This broad definition includes cement, concrete, and glass, in addition to the more traditional fired clay products such as bricks, roof tiles, pottery, and porcelain. The use of ceramics predates recorded history; the emergence of civilization from a primitive state is chronicled in fragments of pottery. No one knows when small vessels were first shaped by human hands from moist clay and left to harden in the heat of the sun. Such containers held nuts, grains, and berries well, but they lost their shape and slumped into formless mud when water was poured into them. Then someone discovered (perhaps by accident) that if clay was placed in the glowing embers of a fire, it became as hard as rock and withstood water well. Molded figures (found in what is now the Czech Republic) that were made 24,000 years ago are the earliest fired ceramic objects discovered so far, and fired clay vessels from the Near East date from 8000 B.C. With the action of fire on clay, the art and science of ceramics began.

Ceramics offer stiffness, hardness, resistance to wear, and resistance to corrosion (particularly by oxygen and water), even at high temperature. They are less dense than most metals, which makes them desirable metal substitutes when weight is a factor. Most are good electrical insulators at ordinary temperatures, a property that is exploited in electronics and power transmission. Ceramics retain their strength well at high temperatures. Several important structural metals soften or melt at temperatures 1000°C below the melting points of their chemical compounds in ceramics. Aluminum, for example, melts at 660°C, whereas aluminum oxide (Al_2O_3), an important compound in many ceramics, does not melt until a temperature of 2051°C is reached.

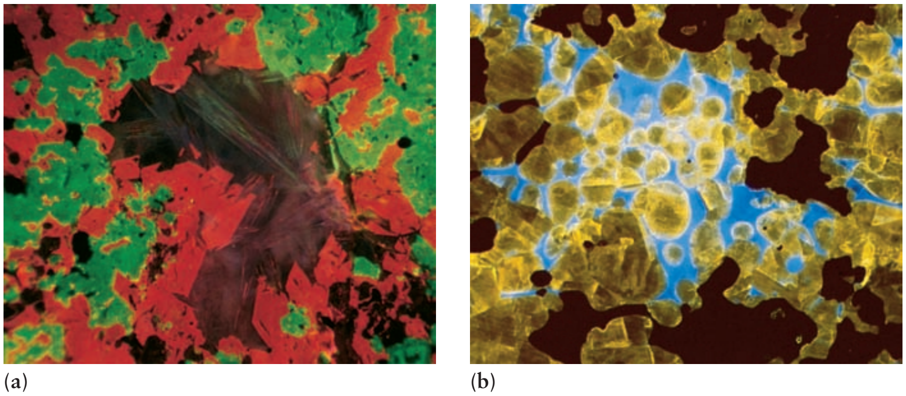
Against these advantages must be listed some serious disadvantages. Ceramics are generally brittle and low in tensile strength. They tend to have high thermal expansion but low thermal conductivity, making them subject to **thermal shock,** in which sudden local temperature change causes cracking or shattering. Metals and plastics dent or deform under stress, but ceramics cannot absorb stress in this way: instead, they break. A major drawback of ceramics as structural materials is their tendency to fail unpredictably and catastrophically in use. Moreover, some ceramics lose mechanical strength as they age, an insidious and serious problem.

Composition and Structure of Ceramics

Ceramics use a variety of chemical compounds, and useful ceramic bodies are nearly always mixtures of several compounds. **Silicate ceramics,** which include the commonplace pots, dishes, and bricks, are made from aluminosilicate clay minerals. All contain the tetrahedral SiO_4 grouping discussed in Section 22.1. In **oxide ceramics,** silicon is a minor or nonexistent component. Instead, a number of metals combine with oxygen to give compounds such as alumina (Al_2O_3), magnesia (MgO), or yttria (Y_2O_3). **Nonoxide ceramics** contain compounds that are free of oxygen as principal components. Some important compounds in nonoxide ceramics are silicon nitride (Si_3N_4), silicon carbide (SiC), and boron carbide (approximate composition B_4C).

One important property of ceramics is their porosity. Porous ceramics have small openings into which fluids (typically air or water) can infiltrate. Fully dense ceramics have no channels of this sort. Two ceramic pieces can have the same chemical composition but quite different densities if the first is porous and the second is not.

A **ceramic phase** is any portion of the whole body that is physically homogeneous and bounded by a surface that separates it from other parts. Distinct phases are visible at a glance in coarse-grained ceramic pieces; in a fine-grained piece, phases can be seen with a microscope. When examined on a still finer scale, most ceramics, like metals, are microcrystalline, consisting of small crystalline grains cemented together (Fig. 22.7). The **microstructure** of such objects includes the sizes and shapes of the grains, the sizes and distribution of voids (openings between grains) and cracks, the identity and distribution of impurity grains, and the presence of stresses within the structure. Microstructural variations have enormous importance in ceramics because slight changes at this level strongly influence the properties of individual ceramic pieces. This is less true for plastic and metallic objects.


(a)
(b)

Musa Karakus and Richard Hagni

FIGURE 22.7 Microstructures of aluminosilicate ceramics, viewed by the different colors of light emitted after bombardment by electrons. (a) Forsterite (red), spinel (green), and periclase (dark brown) grains. (b) Periclase (blue) and oldhamite (yellow) grains.

The microstructure of a ceramic body depends markedly on the details of its fabrication. The techniques of forming and firing a ceramic piece are as important as its chemical composition in determining ultimate behavior because they confer a unique microstructure. This fact calls attention to the biggest problem with ceramics as structural materials: inconsistent quality. Ceramic engineers can produce parts that are stronger than steel, but not reliably so because of the difficulties of monitoring and controlling microstructure. Gas turbine engines fabricated of silicon nitride (Fig. 22.8), for example, run well at 1370°C, which is hot enough to soften or melt most metals. The higher operating temperature increases engine efficiency, and the ceramic turbines weigh less, which further boosts fuel economy. Despite these advantages, there is no commercial ceramic gas turbine. Acceptable ceramic turbines have to be built from selected, pretested components. The testing costs and rejection rates are so high that economical mass production has been impossible so far.

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Making Ceramics

The manufacture of most ceramics involves four steps: (1) the preparation of the raw material; (2) the forming of the desired shape, often achieved by mixing a powder with water or other binder and molding the resulting plastic mass; (3) the drying and firing of the piece, also called its **densification,** because pores (voids) in the dried ceramic fill in; and (4) the finishing of the piece by sawing, grooving, grinding, or polishing.

The raw materials for traditional ceramics are natural clays that come from the earth as powders or thick pastes and become plastic enough after adjustment of their water content to be formed freehand or on a potter's wheel. Special ceramics (both oxide and nonoxide) require chemically pure raw materials that are produced synthetically. Close control of the purity of the starting materials for these ceramics is essential to produce finished pieces with the desired properties. In addition to being formed by hand or in open molds, ceramic pieces are shaped by the squeezing (compacting) of the dry or semidry powders in a strong, closed mold of the desired shape, at either ordinary or elevated temperatures (hot pressing).

Firing a ceramic causes **sintering** to occur. In sintering, the fine particles of the ceramic start to merge together by diffusion at high temperatures. The density of the material increases as the voids between grains are partially filled. Sintering occurs below the melting point of the material and shrinks the ceramic body. In addition to the merging of the grains of the ceramic, firing causes partial melting, chemical reactions among different phases, reactions with gases in the atmosphere of the firing chamber, and recrystallization of compounds with an accompanying growth in crystal size. All of these changes influence the microstructure of a piece and must be understood and controlled. Firing accelerates physical and chemical changes, of course, but thermodynamic equilibrium in a fired ceramic piece is rarely reached. Kinetic factors—including the rate of heating, the length of time at which each temperature is held, and the rate of cooling—influence microstructure. As a result, the use of microwave radiation (as in microwave ovens) rather than kilns to fire ceramics is under development in ceramic factories, because it promises more exact control of the heating rate, and thereby more reliable quality.

22.3 Silicate Ceramics

The silicate ceramics include materials that vary widely in composition, structure, and use. They range from simple earthenware bricks and pottery to cement, fine porcelain, and glass. Their structural strength is based on the same linking of silicate ion tetrahedra that gives structure to silicate minerals in nature.

Pottery and Structural Clay Products

Aluminosilicate clays are products of the weathering of primary minerals. When water is added to such clays in moderate amount, a thick paste results that is easily molded into different shapes. Clays expand as water invades the space between adjacent aluminosilicate sheets of the mineral, but they release most of this water to a dry atmosphere and shrink. A small fraction of the water or hydroxide ions remains rather tightly bound by ion–dipole forces to cations between the aluminosilicate sheets and is lost only when the clay is heated to a high temperature. The firing of aluminosilicate clays simultaneously causes irreversible chemical changes to occur. The clay kaolinite ($Al_2Si_2O_5(OH)_4$) undergoes the following reaction:

$$\underset{\text{(kaolinite)}}{3\ Al_2Si_2O_5(OH)_4} \longrightarrow \underset{\text{(mullite)}}{Al_6Si_2O_{13}(s)} + \underset{\text{(silica)}}{4\ SiO_2(s)} + \underset{\text{(water)}}{6\ H_2O(g)}$$

The fired ceramic body is a mixture of two phases: mullite and silica. Mullite, a rare mineral in nature, takes the form of needlelike crystals that interpenetrate and confer strength on the ceramic. When the temperature is above 1470°C, the silica phase forms as minute grains of cristobalite, one of the several crystalline forms of SiO_2.

If chemically pure kaolinite is fired, the finished ceramic object is white. Such purified clay minerals are the raw material for fine china. As they occur in nature, clays contain impurities, such as transition-metal oxides, that affect the color of both the unfired clay and the fired ceramic object if they are not removed. The colors of the metal oxides arise from their absorption of light at visible wavelengths, as explained by crystal field theory (see Section 8.5). Common colors for ceramics are yellow or greenish yellow, brown, and red. Bricks are red when the clay used to make them has high iron content.

Before a clay is fired in a kiln, it must first be freed of moisture by slowly heating to about 500°C. If a clay body dried at room temperature were to be placed directly into a hot kiln, it would literally explode from the sudden, uncontrolled expulsion of water. A fired ceramic shrinks somewhat as it cools, causing cracks to form. These imperfections limit the strength of the fired object and are undesirable. The occurrence of imperfections can be reduced by coating the surface of a partially fired clay object with a **glaze,** a thin layer that minimizes crack formation in the underlying ceramic by holding it in a state of tension as it cools. Glazes, as their name implies, are glasses that have no sharp melting temperature, but rather harden and develop resistance to shear stresses increasingly as the temperature of the high-fired clay object is gradually reduced. Glazes generally are aluminosilicates that have high aluminum content to raise their viscosity, and thereby reduce the tendency to run off the surface during firing. They also provide the means of coloring the surfaces of fired clays and imparting decorative designs to them. Transition-metal oxides (particularly those of titanium [Ti], vanadium [V], chromium [Cr], manganese [Mn], iron [Fe], cobalt [Co], nickel [Ni], and Cu) are responsible for the colors. The oxidation state of the transition metal in the glaze is critical in determining the color produced and is controlled by regulating the composition of the atmosphere in the kiln; atmospheres rich in oxygen give high oxidation states, and those poor or lacking in oxygen give low oxidation states.

Glass

Glassmaking probably originated in the Near East about 3500 years ago. It is one of the oldest domestic arts, but its beginnings, like those of metallurgy, are obscure. Both required high-temperature, charcoal-fueled ovens and vessels made of materials that did not easily melt to initiate and contain the necessary chemical reactions. In the early period of glassmaking, desired shapes were fabricated by sculpting them from solid chunks of glass. At a later date, molten glass was poured in successive layers over a core of sand. A great advance was the invention of glassblowing, which probably occurred in the first century B.C. A long iron tube was dipped into molten glass and a rough ball of viscous material was caused to accumulate on its end by rotating the tube. Blowing into the iron tube forced the soft glass to take the form of a hollow ball (Fig. 22.9) that could be further shaped into a vessel and severed from the blowing tube with a blade. Artisans in the Roman Empire developed glassblowing to a high degree, but with the decline of that civilization, the skill of glassmaking in Europe deteriorated until the Venetians redeveloped the lost techniques a thousand years later.

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FIGURE 22.9 Handcrafted glassware is trimmed after being blown into the desired shape.

Glasses are amorphous solids of widely varying composition (see Section 21.5 for a discussion of the physical properties of glass). In this chapter, the term *glass* is used in the restricted and familiar sense to refer to materials formed from silica, usually in combination with metal oxides. The absence of long-range order in glasses has the consequence that they are **isotropic**—that is, their physical properties are the same in all directions. This has advantages in technology, including that glasses expand uniformly in all directions with an increase in temperature. The mechanical strength of glass is intrinsically high, exceeding the tensile strength of steel, provided the surface is free of scratches and other imperfections. Flaws in the surface provide sites where fractures can start when the glass is stressed. When a glass object of intricate shape and nonuniform thickness is suddenly cooled, internal stresses are locked in; these stresses may be relieved catastrophically when the object is heated or struck (Fig. 22.10). Slowly heating a strained object to a temperature somewhat below its softening point and holding it there for a while before allowing it to cool slowly is called **annealing;** it gives short-range diffusion of atoms a chance to occur and to eliminate internal stresses.

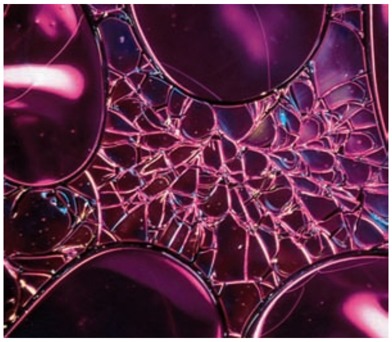

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FIGURE 22.10 The strains associated with internal stresses in rapidly cooled glass can be made visible by viewing the glass in polarized light. They appear as colored regions.

The softening and annealing temperatures of a glass and other properties, such as density, depend on its chemical composition (Table 22.2). Silica itself (SiO_2) forms a glass if it is heated above its melting point and then cooled rapidly to avoid

TABLE 22.2 Composition and Properties of Various Glasses

Silica Glass	Soda-lime Glass	Borosilicate Glass	Aluminosilicate Glass	Leaded Glass
Composition				
SiO_2, 99.9% H_2O, 0.1%	SiO_2, 73% Na_2O, 17% CaO, 5% MgO, 4% Al_2O_3, 1%	SiO_2, 81% B_2O_3, 13% Na_2O, 4% Al_2O_3, 2% B_2O_3, 5%	SiO_2, 63% Al_2O_3, 17% CaO, 8% MgO, 7% Al_2O_3, 2%	SiO_2, 56% PbO, 29% K_2O, 9% Na_2O, 4%
Coefficient of Linear Thermal Expansion ($°C^{-1} \times 10^7$)[†]				
5.5	93	33	42	89
Softening Point (°C)				
1580	695	820	915	630
Annealing Point (°C)				
1050	510	565	715	435
Density ($g\ cm^{-3}$)				
2.20	2.47	2.23	2.52	3.05
Refractive Index[‡] at λ = 589 nm				
1.459	1.512	1.474	1.530	1.560

[†] The coefficient of linear thermal expansion is defined as the fractional increase in length of a body when its temperature is increased by 1°C.

[‡] The refractive index is a vital property of glass for optical applications. It is defined by $n = \sin \theta_i / \sin \theta_r$, where θ_i is the angle of incidence of a ray of light on the surface of the glass and θ_r is the angle of refraction of the ray of light in the glass.

crystallization. The resulting vitreous (glassy) silica has limited use because the high temperatures required to shape it make it quite expensive. Sodium silicate glasses are formed in the high-temperature reaction of silica sand with anhydrous sodium carbonate (soda ash, Na_2CO_3):

$$Na_2CO_3(s) + n\ SiO_2(s) \longrightarrow Na_2O\cdot(SiO_2)_n(s) + CO_2(g)$$

The melting point of the nonvolatile product is about 900°C, and the glassy state results if cooling through that temperature is rapid. The product, called "water glass," is water-soluble; thus, it is unsuitable for making vessels. Its aqueous solutions, however, are used in some detergents and as adhesives for sealing cardboard boxes.

An insoluble glass with useful structural properties results if lime (CaO) is added to the sodium carbonate–silica starting materials. **Soda-lime glass** is the resulting product, with the approximate composition $Na_2O\cdot CaO\cdot(SiO_2)_6$. Soda-lime glass is easy to melt and shape and is used in applications ranging from bottles to window glass. It accounts for more than 90% of all the glass manufactured today. The structure of this ionic glass is shown schematically in Figure 22.11. It is a three-dimensional network of the type discussed in Section 22.1, but with random coordination of the silicate tetrahedra. The network is a giant "polyanion," with Na^+ and Ca^{2+} ions distributed in the void spaces to compensate for the negative charge on the network.

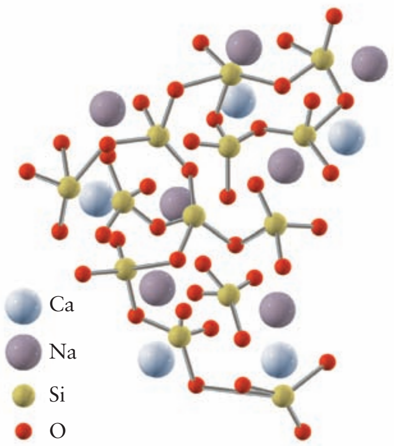

FIGURE 22.11 Structure of a soda-lime glass. Note the tetrahedral coordination of oxygen atoms around each silicon atom.

Replacing lime and some of the silica in a glass by other oxides (Al_2O_3, B_2O_3, K_2O, or PbO) modifies its properties noticeably. For example, the thermal conductivity of ordinary (soda-lime) glass is quite low, and its coefficient of thermal expansion is high. This means that internal stresses are created when its surface is subjected locally to extreme heat or cold, and it may shatter. The coefficient of thermal expansion is appreciably lower in certain borosilicate glasses, in which many of the silicon sites are occupied by boron. Pyrex, the most familiar of these glasses, has a coefficient of linear expansion about one-third that of ordinary soda-lime glass and is the preferred material for laboratory glassware and household ovenware. Vycor has an even smaller coefficient of expansion (approximating that of fused silica) and is made by chemical treatment of a borosilicate glass to leach out its sodium. This leaves a porous structure that is densified by increasing the temperature and shrinking the glass to its final volume.

Cements

Hydraulic cement was first developed by the ancient Romans, who found that a mixture of lime (CaO) and dry volcanic ash reacts slowly with water, even at low temperatures, to form a durable solid. They used this knowledge to build the Pantheon in Rome, a circular building whose concrete dome, spanning 143 feet without internal support, still stands nearly 2000 years after its construction! The knowledge of cement making was lost for centuries after the fall of the Roman Empire. It was rediscovered in 1824 by an English bricklayer, Joseph Aspdin, who patented a process for calcining a mixture of limestone and clay. He called the product **Portland cement** because, when mixed with water, it hardened to a material that resembled a kind of limestone found on the Isle of Portland. Portland cement is now manufactured in every major country, and annual worldwide production is currently about 800 million metric tons, exceeding the production of all other materials. Portland cement opened up a new age in the methods of constructing highways and buildings: Rock could be crushed and then molded in cement, rather than shaped with cutting tools.

Portland cement is a finely ground, powdered mixture of compounds produced by the high-temperature reaction of lime, silica, alumina, and iron oxide. The lime (CaO) may come from limestone or chalk deposits, and the silica (SiO_2) and alumina (Al_2O_3) are often obtained in clays or slags. The blast furnaces of steel mills are a common source of slag, which is a byproduct of the smelting of iron ore.

The composition of slag varies, but it can be represented as a calcium aluminum silicate of approximate formula $CaO{\cdot}Al_2O_3{\cdot}(SiO_2)_2$. Molten slag solidifies into "blast furnace clinkers" on quenching in water. This material is crushed and ground to a fine powder, blended with lime in the correct proportion, and burned again in a horizontal rotary kiln at temperatures up to 1500°C to produce "cement clinker." A final stage of grinding and the addition of about 5% gypsum ($CaSO_4{\cdot}2\ H_2O$) to lengthen the setting time completes the process of manufacture. Table 22.3 presents the composition of a typical Portland cement. Table 22.3 gives percentages of the separate oxides; these simple materials, which are the "elements" of cement making, combine in the cement in more complex compounds such as tricalcium silicate, $(CaO)_3{\cdot}SiO_2$, and tricalcium aluminate, $(CaO)_3{\cdot}Al_2O_3$.

TABLE 22.3 Composition of Portland Cement

Oxide	Percentage by Mass
Lime (CaO)	61–69
Silica (SiO_2)	18–24
Alumina (Al_2O_3)	4–8
Iron(III) oxide (Fe_2O_3)	1–8
Minor oxides (MgO, Na_2O, K_2O, SO_3)	2–4

Cement *sets* when the semiliquid slurry first formed by the addition of water to the powder becomes a solid of low strength. Subsequently, it gains strength in a slower *hardening* process. Setting and hardening involve a complex group of exothermic reactions in which several hydrated compounds form. Portland cement is a **hydraulic cement,** because it hardens not by loss of admixed water, but by chemical reactions that incorporate water into the final body. The main reaction during setting is the hydration of the tricalcium aluminate, which can be approximated by the following equation:

$$(CaO)_3{\cdot}Al_2O_3(s) + 3\,(CaSO_4{\cdot}2H_2O)(s) + 26\ H_2O(\ell) \longrightarrow (CaO)_3{\cdot}Al_2O_3{\cdot}(CaSO_4)_3{\cdot}32H_2O(s)$$

The product forms after 5 or 6 hours as a microscopic forest of long crystalline needles that lock together to solidify the cement. Later, the calcium silicates react with water to harden the cement. For example:

$$6\,(CaO)_3{\cdot}SiO_2(s) + 18\ H_2O(\ell) \longrightarrow (CaO)_5{\cdot}(SiO_2)_6{\cdot}5H_2O(s) + 13\ Ca(OH)_2(s)$$

The hydrated calcium silicates develop as strong tendrils that coat and enclose unreacted grains of cement, each other, and other particles that may be present, binding them in a robust network. Most of the strength of cement comes from these entangled networks, which, in turn, depend ultimately for strength on chains of O—Si—O—Si silicate bonds. Hardening is slower than setting; it may take as long as 1 year for the final strength of a cement to be attained.

Portland cement is rarely used alone. Generally, it is combined with sand, water, and lime to make **mortar,** which is applied with a trowel to bond bricks or stone together in an assembled structure. When Portland cement is mixed with sand and aggregate (crushed stone or pebbles) in the proportions of 1 : 3.75 : 5 by volume, the mixture is called **concrete.** Concrete is outstanding in its resistance to compressive forces and is therefore the primary material in use for the foundations of buildings and the construction of dams, in which the compressive loads are enormous. The stiffness (resistance to bending) of concrete is high, but its fracture toughness (resistance to impact) is substantially lower and its tensile strength is relatively poor. For this reason, concrete is usually reinforced with steel rods when it is used in structural elements such as beams that are subject to transverse or tensile stresses.

As excess water evaporates from cement during hardening, pores form that typically comprise 25% to 30% of the volume of the solid. This porosity weakens concrete, and recent research has shown that the fracture strength is related inversely to the size of the largest pores in the cement. A new material, called "macro defect–free" (MDF) cement, has been developed in which the size of the pores is reduced from about a millimeter to a few micrometers by the addition of water-soluble polymers that make a doughlike "liquid" cement that is moldable with the use of far less water. Unset MDF cement is mechanically kneaded and extruded into the desired shape. The final result possesses substantially increased bending resistance and fracture toughness. MDF cement can even be molded into springs and shaped on a conventional lathe. When it is reinforced with organic fibers, its toughness is further increased. The development of MDF cement is a good illustration of the way in which chemistry and engineering collaborate to furnish new materials.

22.4 Nonsilicate Ceramics

Many useful ceramics exist that are *not* based on the Si—O bond and the SiO_4 tetrahedron. They have important uses in electronics, optics, and the chemical industry. Some of these materials are oxides, but others contain neither silicon nor oxygen.

Oxide Ceramics

Oxide ceramics are materials that contain oxygen in combination with any of a number of metals. These materials are named by adding an *-ia* ending to the stem of the name of the metallic element. Thus, if the main chemical component of an oxide ceramic is Be_2O_3, it is a *beryllia* ceramic; if the main component is Y_2O_3, it is an *yttria* ceramic; and if it is MgO, it is a *magnesia* ceramic. As Table 22.4 shows, the melting points of these and other oxides are substantially higher than the melting points of the elements themselves. Such high temperatures are hard to achieve and maintain, and the molten oxides corrode most container materials. Oxide ceramic bodies are therefore not shaped by melting the appropriate oxide and pouring it into a mold. Instead, these ceramics are fabricated by sintering, like the silicate ceramics.

Alumina (Al_2O_3) is the most important nonsilicate ceramic material. It melts at a temperature of 2051°C and retains strength even at temperatures of 1500°C to 1700°C. Alumina has a large electrical resistivity and withstands both thermal shock and corrosion well. These properties make it a good material for spark plug insulators, and most spark plugs now use a ceramic that is 94% alumina.

High-density alumina is fabricated in such a way that open pores between the grains are nearly completely eliminated; the grains are small, with an average diameter as low as 1.5 μm. Unlike most others, this ceramic has good mechanical strength against impact, which has led to its use in armor plating. The ceramic absorbs the energy of an impacting projectile by breaking; thus, penetration does not occur. High-density alumina is also used in high-speed cutting tools for machining metals. The temperature resistance of the ceramic allows much faster cutting speeds, and a ceramic cutting edge has no tendency to weld to the metallic work piece, as metallic tools do. These properties make alumina cutting tools superior to metallic tools, as long as they do not break too easily. High-density alumina is also used in artificial joints (Fig. 22.12).

If Al_2O_3 doped with a small percentage of MgO is fired in a vacuum or a hydrogen atmosphere (instead of air) at a temperature of 1800°C to 1900°C, even very small pores, which scatter light and make the material white, are removed. The resulting ceramic is translucent. This material is used to contain the sodium in high-intensity sodium discharge lamps. With envelopes of high-density alumina, these lamps can be operated at temperatures of 1500°C to give a whiter and more intense light. Old-style sodium-vapor lamps with glass envelopes were limited to a temperature of 600°C because the sodium vapor reacted with the glass at higher


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FIGURE 22.12 Socket in this artificial hip is made of high-density alumina.

TABLE 22.4 Melting Points of Some Metals and Their Oxides

Metal	Melting Point (°C)	Oxide	Melting Point (°C)
Be	1287	BeO	2570
Mg	651	MgO	2800
Al	660	Al_2O_3	2051
Si	1410	SiO_2	1723
Ca	865	CaO	2572
Y	1852	Y_2O_3	2690

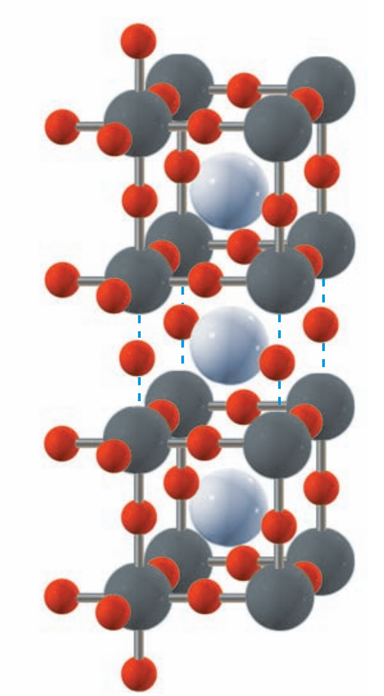

FIGURE 22.13 Structure of perovskite ($CaTiO_3$). A stack of three unit cells is shown, with some additional O atoms (red) from neighboring cells. Each Ti atom (gray) is surrounded by six O atoms; each Ca atom (white) has eight O atoms as nearest neighbors.

temperatures. At low temperatures, the light from a sodium-vapor lamp has an undesirable yellow color.

Magnesia (MgO) is mainly used as a **refractory**—a ceramic material that withstands a temperature of more than 1500°C without melting (MgO melts at 2800°C). A major use of magnesia is as insulation in electrical heating devices, because it combines high thermal conductivity with excellent electrical resistance. Magnesia is prepared from magnesite ores, which consist of $MgCO_3$ and a variety of impurities. When purified magnesite is heated to 800°C to 900°C, carbon dioxide is driven off to form $MgO(s)$ in fine grains:

$$MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$$

After cooling, fine-grained MgO reacts vigorously with water to form magnesium hydroxide:

$$MgO(s) + H_2O(\ell) \longrightarrow Mg(OH)_2(s)$$

Heating fine-grained $MgO(s)$ to 1700°C causes the MgO grains to sinter, giving a "dead-burned magnesia" that consists of large crystals and does not react with water. The $\Delta G°$ of the reaction between MgO and H_2O does not change when magnesia is dead burned. The altered microstructure (larger crystals vs small) makes the reaction with water exceedingly slow, however.

Superconducting Ceramics

The oxide ceramics discussed so far in this chapter all consisted of single chemical compounds, except for minor additives. A natural idea for new ceramics is to make materials that contain two (or more) oxides in equal or nearly equal molar amounts. Thus, if $BaCO_3$ and TiO_2 are mixed and heated to high temperature, they react to give the ceramic barium titanate:

$$BaCO_3(s) + TiO_2(s) \longrightarrow BaTiO_3(s) + CO_2(g)$$

Barium titanate, which has many novel properties, is a **mixed oxide ceramic.** It has the same structure as the mineral **perovskite,** $CaTiO_3$ (Fig. 22.13), except, of course, that Ba replaces Ca. Perovskites typically have two metal atoms for every three O atoms, giving them the general formula ABO_3, where A stands for a metal atom at the center of the unit cube and B stands for an atom of a different metal at the cube corners.

Research interest in perovskite ceramic compositions has grown explosively after the discovery that some of them become **superconducting** at relatively high temperatures. A superconducting material offers no resistance whatsoever to the flow of an electric current. The phenomenon was discovered by the Dutch physicist Heike Kamerlingh-Onnes in 1911, when he cooled mercury below its superconducting transition temperature of 4 K. Such low temperatures are difficult to achieve and maintain, but if practical superconductors could be made to work at higher temperatures (or even at room temperature!), then power transmission, electronics, transportation, medicine, and many other aspects of human life would be transformed. More than 60 years of research with metallic systems culminated in 1973 with the discovery of a niobium–tin alloy with a world-record superconducting transition temperature of 23.3 K. Progress toward higher temperature superconductors then stalled until 1986, when K. Alex Müller and J. Georg Bednorz, who had had the inspired notion to look for higher transition temperatures among perovskite ceramics, found a Ba—La—Cu—O perovskite phase having a transition temperature of 35 K. This result motivated other scientists, who soon discovered another rare-earth–containing perovskite ceramic that became a superconductor at 90 K. This result was particularly exciting because 90 K exceeds the boiling point of liquid nitrogen (77 K), a relatively cheap refrigerant (Fig. 22.14). This 1-2-3 compound (so called because its formula, $YBa_2Cu_3O_{(9-x)}$,

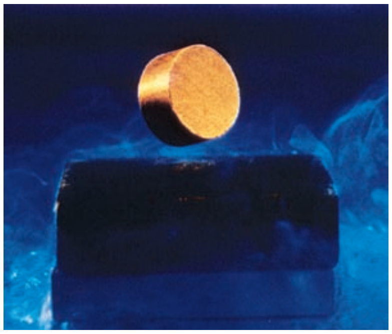

FIGURE 22.14 Levitation of a small magnet above a disk of superconducting material. A superconducting substance cannot be penetrated by an external magnetic field. At room temperature, the magnet rests on the ceramic disk. When the disk is cooled with liquid nitrogen, it becomes superconducting and excludes the magnet's field, forcing the magnet into the air.

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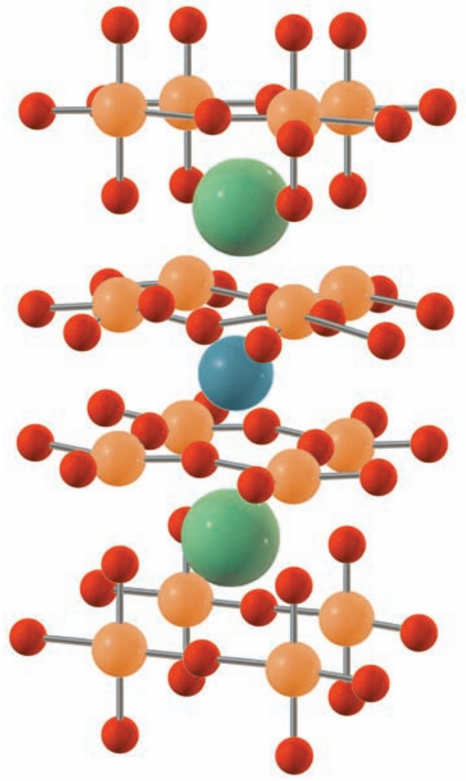

FIGURE 22.15 The structure of $YBa_2Cu_3O_{9-x}$ is a layered perovskite. Each Cu atom (orange) is bonded to O atoms (red). The layers differ because one-third of them contain Y atoms (blue-gray), whereas two-thirds contain Ba atoms (green). This structure is a variation of the perovskite structure in Figure 22.13. In a hypothetical "$BaCuO_3$" structure, every third Ba has been replaced by a Y, and the O atoms in the layer containing the Y have been removed. Note that the Cu—O layers above and below the Y atom are puckered.

has one Y, two Ba, and three Cu atoms per formula unit) is not an ideal perovskite because it has fewer than nine O atoms in combination with its six metal atoms. The deficiency makes x in the formula somewhat greater than 2, depending on the exact method of preparation. The structure of this nonstoichiometric solid is shown in Figure 22.15. More recently, the maximum superconducting transition temperature has increased to 125 K in another class of ceramics that does not contain rare-earth elements.

A crucial concern in the application of superconducting ceramics is to devise ways to fabricate the new materials in desired shapes such as wires. This will be quite a challenge because these superconductors are ceramics and have the brittleness and fragility typical of ceramic materials.

Nonoxide Ceramics

In nonoxide ceramics, nitrogen (N) or carbon (C) takes the place of oxygen in combination with silicon or boron. Specific substances are boron nitride (BN), boron carbide (B_4C), the silicon borides (SiB_4 and SiB_6), silicon nitride (Si_3N_4), and silicon carbide (SiC). All of these compounds possess strong, short covalent bonds. They are hard and strong, but brittle. Table 22.5 lists the enthalpies of the chemical bonds in these compounds.

Much research has aimed at making gas-turbine and other engines from ceramics. Of the oxide ceramics, only alumina and zirconia (ZrO_2) are strong enough, but both resist thermal shock too poorly for this application. Attention has therefore turned to the nonoxide **silicon nitride** (Si_3N_4). In this **network solid** (Fig. 22.16), every Si atom bonds to four N atoms that surround it at the corners of a tetrahedron; these tetrahedra link into a three-dimensional network by sharing corners. The Si—N bond is covalent and strong (the bond enthalpy is 439 kJ mol^{-1}). The similarity to the joining of SiO_4 units in silicate minerals (see Section 22.1) is clear.

TABLE 22.5 Bond Enthalpies in Nonoxide Ceramics

Bond	Bond Enthalpy ($kJ\ mol^{-1}$)
B—N	389
B—C	448
Si—N	439
Si—C	435
B—Si	289
C—C	350

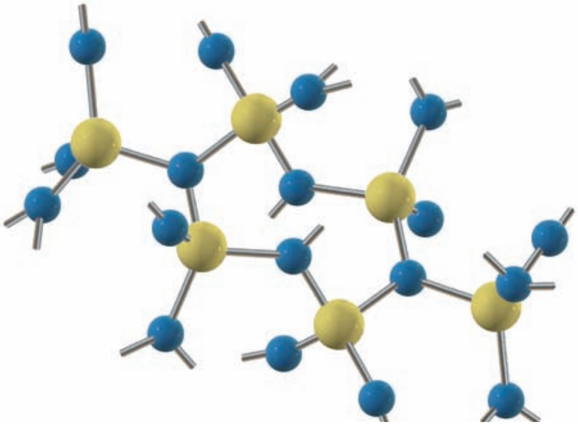

FIGURE 22.16 Structure of silicon nitride (Si_3N_4). Each Si atom is bonded to four N atoms, and each N atom is bonded to three Si atoms. The result is a strong network.

At first, silicon nitride appears chemically unpromising as a high-temperature structural material. It is unstable in contact with water because the following reaction has a negative $\Delta G°$:

$$Si_3N_4(s) + 6\ H_2O(\ell) \longrightarrow 3\ SiO_2(s) + 4\ NH_3(g)$$

In fact, this reaction causes finely ground Si_3N_4 powder to give off an odor of ammonia in moist air at room temperature. Silicon nitride is also thermodynamically unstable in air, reacting spontaneously with oxygen:

$$Si_3N_4(s) + 3\ O_2(g) \longrightarrow 3\ SiO_3(s) + 2\ N_2(g)$$

The reaction has a $\Delta G°$ of -1927 kJ mol^{-1}. In practice, neither reaction occurs at a perceptible rate when Si_3N_4 is in bulk form. Initial contact of oxygen or water with $Si_3N_4(s)$ forms a surface film of $SiO_2(s)$ that protects the bulk of the $Si_3N_4(s)$ from further attack. When *strongly* heated in air (to about 1900°C), Si_3N_4 does decompose, violently, but until that temperature is reached, it resists attack.

Fully dense silicon nitride parts are stronger than metallic alloys at high temperatures. Ball bearings made of dense silicon nitride work well without lubrication at temperatures up to 700°C; for example, they last longer than steel ball bearings. Because the strength of silicon nitride increases with the density attained in the production process, the trick is to form a dense piece of silicon nitride in the desired shape. One method for making useful shapes of silicon nitride is "reaction bonding." Powdered silicon is compacted in molds, removed, and then fired under an atmosphere of nitrogen at 1250°C to 1450°C. The following reaction forms the ceramic:

$$3\ Si(s) + 2\ N_2(g) \longrightarrow Si_3N_4(s)$$

The parts neither swell nor shrink significantly during the chemical conversion from Si to Si_3N_4, making it possible to fabricate complex shapes reliably. Unfortunately, reaction-bonded Si_3N_4 is still somewhat porous and is not strong enough for many applications. In the "hot-pressed" forming process, Si_3N_4 powder is prepared in the form of exceedingly small particles by reaction of silicon tetrachloride with ammonia:

$$3\ SiCl_4(g) + 4\ NH_3(g) \longrightarrow Si_3N_4(s) + 12\ HCl(g)$$

The solid Si_3N_4 forms as a smoke. It is captured as a powder, mixed with a carefully controlled amount of MgO additive, placed in an enclosed mold, and sintered at 1850°C under a pressure of 230 atm. The resulting ceramic shrinks to nearly full density (no pores). Because the material does not flow well (to fill a complex mold completely), only simple shapes are possible. Hot-pressed silicon nitride is impressively tough and can be machined only with great difficulty and with diamond tools.

In the silicate minerals of Section 22.1, AlO_4^{5-} units routinely substitute for SiO_4^{4-} tetrahedra as long as positive ions of some type are present to balance the electric charge. This fact suggests that in silicon nitride some Si^{4+} ions, which lie at the centers of tetrahedra of N atoms, could be replaced by Al^{3+} if a compensating replacement of O^{2-} for N^{3-} were simultaneously made. Experiments show that ceramic alloying of this type works well, giving many new ceramics with great potential called **sialons** (named for the four elements Si—Al—O—N). These ceramics illustrate the way a structural theme in a naturally occurring material guided the search for new materials.

Boron has one fewer valence electron than carbon, and nitrogen has one more valence electron. **Boron nitride** (BN) is therefore isoelectronic with C_2, and it is not surprising that it has two structural modifications that resemble the structures of graphite and diamond. In hexagonal boron nitride, the B and N atoms take alternate places in an extended "chicken-wire" sheet in which the B—N distance is 1.45 Å. The sheets stack in such a way that each B atom has a N atom directly above it and directly below it, and vice versa. The cubic form of boron nitride has the diamond structure, is comparable in hardness to diamond, and resists oxidation better. Boron nitride is often prepared by **chemical vapor deposition,** a method used in fabricating several other ceramics as well. In this method, a controlled chemical reaction of gases on a contoured, heated surface gives a solid product of the desired shape. If a cup made of BN is needed, a cup-shaped mold is heated to a temperature exceeding 1000°C and a mixture of $BCl_3(g)$ and $NH_3(g)$ is passed over its surface. The reaction

$$BCl_3(g) + NH_3(g) \longrightarrow BN(s) + 3\,HCl(g)$$

deposits a cup-shaped layer of BN(*s*). Boron nitride cups and tubes are used to contain and evaporate molten metals.

Silicon carbide (SiC) is diamond in which half of the C atoms are replaced by Si atoms. Also known by its trade name of Carborundum, silicon carbide was developed originally as an abrasive, but it is now used primarily as a refractory and as an additive in steel manufacture. It is formed and densified by methods similar to those used with silicon nitride. Silicon carbide is often produced in the form of small plates or whiskers to reinforce other ceramics. Fired silicon carbide whiskers are quite small (0.5 μm in diameter and 50 μm long) but are strong. They are mixed with a second ceramic material before that material is formed. Firing then gives a **composite ceramic.** Such composites are stronger and tougher than unreinforced bodies of the same primary material. Whiskers serve to reinforce the main material by stopping cracks; they either deflect advancing cracks or soak up their energy, and a widening crack must dislodge them to proceed (Fig. 22.17). Recently, SiC has been used in high power, high temperature semiconductor devices (Section 22.7).

22.5 Electrical Conduction in Materials

Electronic properties describe the movement of charged particles in a material in response to an applied electric field. If the charges are free to move throughout the material, the process is *electrical conduction,* measured by the *electrical conductivity* of the material. Differences in the magnitude of the conductivity distinguish metals, semiconductors, and insulators. If the charges can move only limited distances and are then halted by opposing binding forces, separation of positive and negative charges leads to *electric polarization* of the material, measured by its *dielectric constant*. Conduction involves dissipation of energy as heat, whereas polarization involves storage of potential energy in the material.

An electric field applied to a material that has free charged particles causes these particles to flow through the material and into the external circuit. How do we define and measure the conductivity of a material? On what macroscopic properties does it depend? How does it relate to the detailed chemical structure of the material?

Measurement of Conductivity

The electrical conductivity of a material is measured by placing a cylindrical sample of cross-sectional area, A, and length, ℓ, in a simple electrical circuit as a resistor in series with a power supply and ammeter; a voltmeter measures the actual voltage across the sample (Fig. 22.18). If the voltage, V, is varied and the resulting current, I, is measured at each voltage, a plot of I versus V is a straight line (Fig. 22.19):

$$I = GV \tag{22.1}$$

The resulting slope is called the **conductance** and is denoted by G. If V is measured in volts and I in amperes (A), then G has units of siemens (1 siemens = 1 A/V). If the value of G is constant, the material follows Ohm's law

$$V = IR$$

and G is the reciprocal of the **resistance** R, which is measured in ohms (Ω; 1 Ω = 1 V/A). So far, the measurement depends on the size and shape of the material sample, in addition to its composition. To remove these geometric effects, we note from experiment that R increases as ℓ increases, and it decreases as A increases.

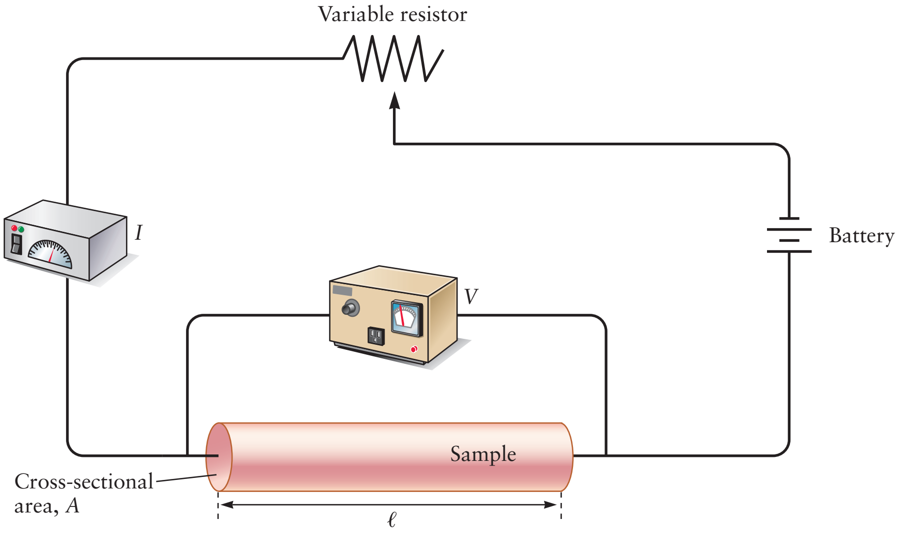

FIGURE 22.18 Test circuit for measuring conductivity.

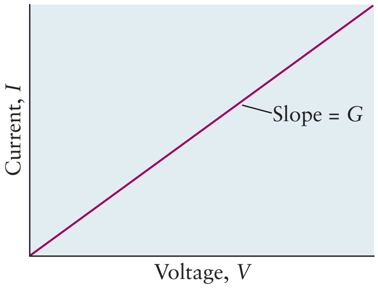

FIGURE 22.19 Plot of current against voltage is a straight line whose slope is the conductance *G*.

Therefore, we define the material property **resistivity,** denoted by ρ, as the proportionality constant that summarizes these two effects:

$$R = \frac{\ell}{A}\rho \tag{22.2}$$

From this definition, ρ has dimensions of Ω m. Finally, we define the material property **conductivity,** σ, as the reciprocal of the resistivity:

$$\sigma = \frac{1}{\rho} = \frac{\ell}{RA} \tag{22.3}$$

from which σ has units of $(\Omega\ \text{m})^{-1}$ or S m^{-1}. We now rewrite Ohm's law in a form independent of sample geometry. First, define the current density $J(\text{A m}^{-2})$ through the sample as I/A and define the electric field $E(\text{V m}^{-1})$ through the sample as V/ℓ. Inserting these definitions and the definition of σ from Equation 22.3 into Equation 22.1 gives:

$$J = \sigma E \tag{22.4}$$

According to Equation 22.4, the current density flowing through a material sample is proportional to the electric field applied to the sample, and the proportionality constant is the conductivity of the material of which the sample is made. This is the equation we use to relate the conductivity of a material to its microstructural properties. Table 22.6 lists conductivities for several common metals at room temperature.[2]

TABLE 22.6 **Electrical Conductivity of Selected Metals at Room Temperature**

Metal	Conductivity $[(\Omega\ \text{m})^{-1}]$
Silver	6.8×10^7
Copper	6.0×10^7
Gold	4.3×10^7
Aluminum	3.8×10^7
Iron	1.0×10^7
Platinum	0.94×10^7
Stainless steel	0.2×10^7

Microscopic Origins of the Conductivity

Insight into the conductivity is provided by measuring the electrical conductivity of aqueous ionic solutions (Fig. 22.20; this topic is referred to in Chapters 11 and 15). The conductivity of pure water, multiply distilled to remove all impurities, is about $0.043 \times 10^{-6}\ (\Omega\ \text{cm})^{-1}$. Exposed to the air, pure water dissolves CO_2, which forms carbonic acid, H_2CO_3; dissociation produces H_3O^+ and HCO_3^-, which increase the conductivity to about $1 \times 10^{-6}\ (\Omega\ \text{cm})^{-1}$. As ionic solutes are added to water, the conductivity increases rapidly; a 1.0-M solution in NaOH has conductivity of about $0.180\ (\Omega\ \text{cm})^{-1}$ at 25°C. The conductivity depends strongly on both concentration and ionic species. The concentration dependence is summarized by the **molar**

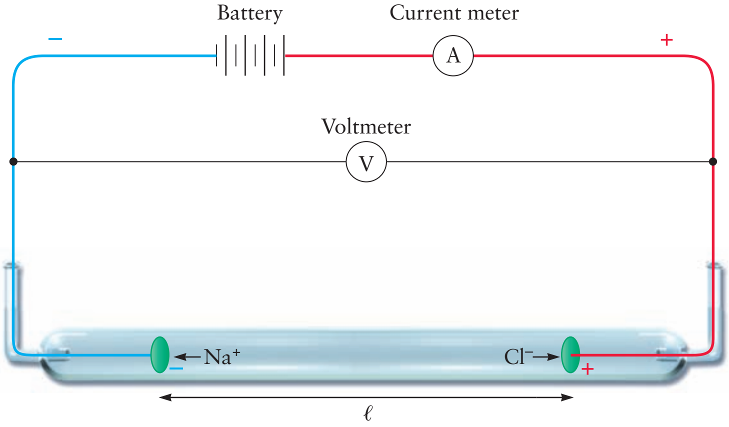

FIGURE 22.20 Apparatus for measuring the conductivity of an aqueous solution of NaCl.

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[2] Because the meter is inconveniently large for measuring the dimensions of most samples in material studies, you will frequently see ρ expressed in units of Ω cm and σ in units of $(\Omega\ \text{cm})^{-1}$. Be alert to the actual units used. In base International System of Units (SI), resistivity has units expressed as kg $\text{m}^3\ \text{s}^{-3}\ \text{A}^{-2}$.

conductivity, defined by $\Lambda_m = \sigma/c$, where c is the concentration of the ion measured in moles per liter. To gain fundamental understanding of the conduction mechanism, we relate Λ_m to the details of the ionic motion in dilute solutions in response to the electric field. This leads to the concept of *mobility* of the ion, denoted by μ, which shows how its surroundings influence the response of an ion to an applied field.

As the electric field is turned on, each ion is accelerated by the field and experiences a force whose magnitude and direction are given by the vector relation

$$\vec{F} = ze\vec{E}$$

where z is the charge on the ion in units of the elementary charge, e, and the expression is valid for either cations or anions (the force points in opposite directions in the two cases). As the ion is accelerated by the field, however, its forward motion is retarded by friction from the surrounding solvent molecules. This retarding force $\vec{F}'$ opposes the direction of motion of the ion and is proportional to its velocity, $\vec{v}$:

$$\vec{F}' = -f\vec{v}$$

where f is the frictional drag coefficient. In due course, these forces balance and the ion achieves its steady drift velocity $\vec{v}_d$. This force balance condition provides the following relation:

$$\vec{v}_d = ze\frac{\vec{E}}{f}$$

This equation shows that the electric field increases the drift velocity, whereas the drag coefficient reduces it. We define the proportionality constant between the *drift speed* (the magnitude of the drift velocity) and the field to be the **mobility,** μ, of the ion (a positive number), giving the following relation:

$$|\vec{v}_d| = \mu|\vec{E}| \qquad [22.5]$$

Mobility has physical units of $\mathrm{m^2\ V^{-1}\ s^{-1}}$. For ions in solution, the mobility is given by

$$\mu = \frac{|z|e}{f}$$

In more advanced work, it is possible to estimate the drag coefficient, f, and provide a theoretical prediction of the mobility. Experimentally, the mobility for ions is obtained from the molar conductivity through the following equation, which we do not justify:

$$\Lambda_m = |z|\mu\mathcal{F} \qquad [22.6]$$

where $\mathcal{F}$ is the Faraday constant, 96,485.34 C $\mathrm{mol^{-1}}$ (the Faraday constant is introduced in Chapter 17).

Mobilities are shown in Table 22.7 for several ions in aqueous solution. One interesting feature is that the smaller cations have lower mobilities than the larger cations; for example, μ for Na^+ is smaller than that for K^+, and μ for Mg^{2+} is smaller than that for Ca^{2+}. One might expect that the smaller ions would have larger mobility, because their smaller size should encounter less frictional drag when moving through the solvent. However, the greater charge density on the smaller cations attracts a larger solvation shell than occurs on the larger cations (see Section 11.2 and Figure 11.4). The entity moving through the solution in response to the electric field is not the "bare" cation but the cation "dressed" with its solvation shell. The larger solvation shell on the smaller ions causes more frictional drag and lower mobility.

It can be shown that the conductivity of an ion is related to its mobility by the following equation:

$$\sigma_{\text{ion}} = |z|en_{\text{ion}}\,\mu_{\text{ion}} \qquad [22.7]$$

TABLE 22.7 Mobilities of Selected Ions in Aqueous Solution at 25°C

Ion	Mobility ($\mathrm{cm^2\ V^{-1}\ s^{-1}}$)
Li^+	4.01×10^{-4}
Na^+	5.19×10^{-4}
K^+	7.62×10^{-4}
Mg^{2+}	5.50×10^{-4}
Ca^{2+}	6.17×10^{-4}
Ba^{2+}	6.60×10^{-4}
Cl^-	7.91×10^{-4}
Br^-	8.10×10^{-4}
NO_3^-	7.40×10^{-4}
ClO_4^-	6.98×10^{-4}
CH_3COO^-	4.24×10^{-4}

where n_{ion} is the number density of ions present, expressed in number per cubic meter. The conductivity depends on two fundamental microscopic variables: the number density of carriers and the carrier mobility. Both positive and negative ions can respond to the electric field in the solution, so the total conductivity must include a contribution from each:

$$\sigma_{\text{tot}} = |z_{\text{cation}}| e n_{\text{cation}} \mu_{\text{cation}} + |z_{\text{anion}}| e n_{\text{anion}} \mu_{\text{anion}} \qquad [22.8]$$

Equations 22.7 and 22.8 are valid for all electrical conduction processes: motion of positive and negative ions in solution and in ionic solids, and motion of electrons in solids. These equations are used in subsequent sections to discuss conduction in a variety of materials. These equations should remind you that the conductivity in any material depends on two separate microscopic parameters: the number of charge carriers present and their mobilities.

EXAMPLE 22.2

The molar conductivity of Na^+ ions in aqueous solution at 25°C has been determined to be 5.01×10^{-2} $(\Omega\ \text{cm})^{-1}$ mol^{-1} L. Assume an electric field of 1.0×10^2 V cm^{-1} is applied to the solution. Calculate the mobility and the drift velocity of Na^+ ions.

SOLUTION

From Equation 22.6, the mobility and molar conductivity are related by

$$\mu = \frac{\Lambda_m}{|z|\mathcal{F}} = \frac{5.01 \times 10^{-2}\ \Omega^{-1}\ \text{cm}^{-1}\ \text{mol}^{-1}\ \text{L}}{(1)(96{,}485\ \text{C mol}^{-1})} = 5.19 \times 10^{-4}\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$$

We used Ohm's law $V = IR$ or $V = \text{C s}^{-1}\ \Omega$ to simplify the units, and we took 1 L = 10^3 cm^3.

From Equation 22.5, the drift velocity is given by

$$v_d = \mu E = (5.19 \times 10^{-4}\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1})(1.0 \times 10^2\ \text{V cm}^{-1}) = 5.19 \times 10^{-2}\ \text{cm s}^{-1}$$

Related Problems: 21, 22, 23, 24, 25, 26

Illustration: Conductivity in Metals

Before the quantum theory of solids (see description in Chapter 21), microscopic descriptions of metals were based on the Drude model, named for the German physicist Paul Drude. The solid was viewed as a fixed array of positively charged metal ions, each localized to a site on the solid lattice. These fixed ions were surrounded by a sea of mobile electrons, one contributed by each of the atoms in the solid. The number density of the electrons, n_{el}, is then equal to the number density of atoms in the solid. As the electrons move through the ions in response to an applied electric field, they can be scattered away from their straight-line motions by collisions with the fixed ions; this influences the mobility of the electrons. As temperature increases, the electrons move more rapidly and the number of their collisions with the ions increases; therefore, the mobility of the electrons decreases as temperature increases. Equation 22.7 applied to the electrons in the Drude model gives

$$\sigma_{\text{el}} = e n_{\text{el}} \mu_{\text{el}} \qquad [22.9]$$

which predicts that the electrical conductivity of a metal will decrease as temperature increases, because the electron mobility decreases with temperature whereas the electron number density is independent of temperature. This simple model prediction agrees with the experimental fact that the resistivity of metals increases as temperature increases.

22.6 Band Theory of Conduction

The characteristic property of metals is their good ability to conduct electricity and heat. Both phenomena are due to the ease with which valence electrons move; electrical conduction is a result of the flow of electrons from regions of high potential energy to those of low potential energy, and heat conduction is a result of the flow of electrons from high-temperature regions (where their kinetic energies are high) to low-temperature regions (where their kinetic energies are low). Why are electrons so mobile in a metal but so tightly bound to atoms in an insulating solid, such as diamond or sodium chloride?

Figure 21.19 shows how the quantum energy levels of Na atoms in a crystal are spread out into a continuous band of states, which is half occupied by electrons. Now, suppose a small electric potential difference is applied across a sodium crystal. The spin-paired electrons that lie deep in the band cannot be accelerated by a weak electric field because occupied levels exist just above them. They have no place to go (recall the Pauli principle, which states that an energy level contains at most two electrons). At the top of the "sea" of occupied levels, however, there is an uppermost electron-occupied or half-occupied level called the **Fermi level.** Electrons that lie near that level have the highest kinetic energy of all the valence electrons in the crystal and can be accelerated by the electric field to occupy the levels above. They are free to migrate in response to the electric field so that they conduct an electric current. These same electrons at the Fermi level are responsible for the high thermal conductivities of metals. They are also the electrons freed by the photoelectric effect when a photon gives them sufficient kinetic energy to escape from the metal (see Section 4.4).

A natural question arises: Why are the alkaline-earth elements metals, given the argument just presented? A metal such as magnesium contains two $3s$ electrons, and one might expect the band derived from the broadened $3s$ level to be completely filled. The answer to this question is that the energies of the $3s$ orbitals and $3p$ orbitals for magnesium are not greatly different. When the internuclear separation becomes small enough, the $3p$ band overlaps the $3s$ band, and many unoccupied sublevels are then available above the highest filled level.

Band Picture of Bonding in Silicon

An analogous procedure to that shown in Figure 21.19 can be used to construct a band picture for silicon. In this case, the $4N_A$ valence atomic orbitals (both $3s$ and $3p$) from 1 mol (N_A atoms) silicon split into *two* bands in the silicon crystal, each containing $2N_A$ closely spaced levels (Fig. 22.21). The lower band is called the **valence band** and the upper one the **conduction band.** Between the top of the valence band and the bottom of the conduction band is an energy region that is forbidden to electrons. The magnitude of the separation in energy between the valence band and the lowest level of the conduction band is called the **band gap,** E_g, which for pure silicon is 1.94×10^{-19} J. This is the amount of energy that an electron must gain to be excited from the top of the valence band to the bottom of the conduction band. For 1 mol of electrons to be excited in this way, the energy is larger by a factor of Avogadro's number N_A, giving 117 kJ mol^{-1}. (Another unit used for band gaps is the *electron volt,* defined in Section 3.2 as 1.60218×10^{-19} J. In this unit, the band gap in Si is 1.21 eV.)

Each Si atom in the crystal contributes four valence electrons to the bands of orbitals in Figure 22.21, for a total of $4N_A$ per mole. This is a sufficient number to place two electrons in each level of the valence band (with opposing spins) and leave the conduction band empty. There are no low-lying energy levels for those

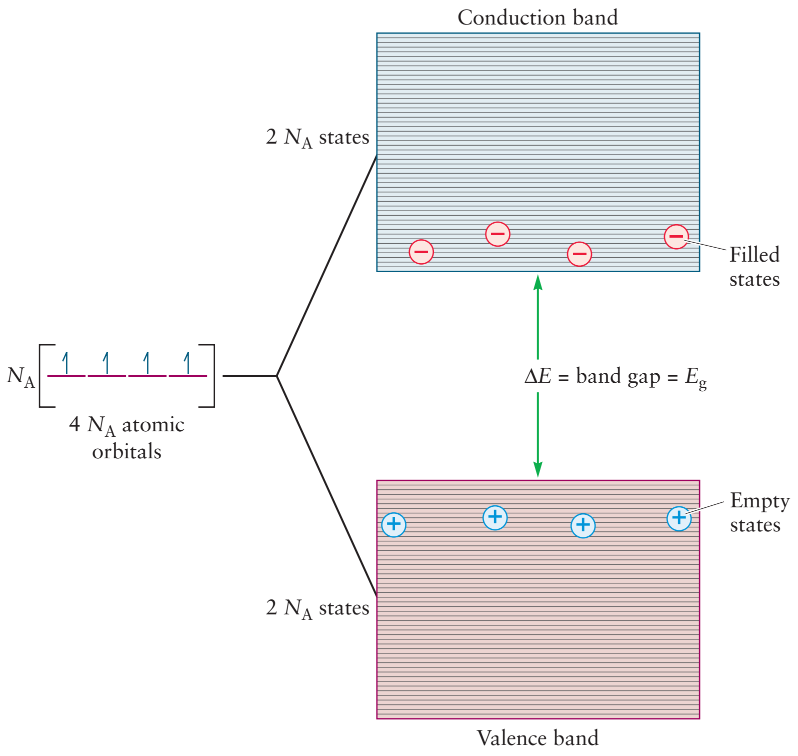


FIGURE 22.21 The valence orbitals of the silicon atom combine in crystalline silicon to give two bands of closely spaced levels. The valence band is almost completely filled, and the conduction band is almost empty.

electrons at the top of the valence band to enter if given a small increment in their energy. The band gap means that an electron at the top of the filled valence band must acquire an energy of at least 1.94×10^{-19} J, equivalent to 117 kJ mol^{-1}, to jump to the lowest empty level of the conduction band. This is a large amount of energy. If it were to be supplied by a thermal source, the temperature of the source would have to be on the order of

$$T = \frac{\Delta E}{R} = \frac{117{,}000 \text{ J mol}^{-1}}{8.315 \text{ J K}^{-1} \text{ mol}^{-1}} = 14{,}000 \text{ K}$$

which is far above the temperature at which a crystalline sample could exist. At room temperature, only a few electrons per mole in the extreme tail of the Boltzmann distribution have enough energy to jump the gap; therefore, the conduction band in pure silicon is sparsely populated with electrons. The result is that silicon is not a good conductor of electricity; good electrical conductivity requires a net motion of many electrons under the impetus of a small electric potential difference. Silicon has an electrical conductivity that is 11 orders of magnitude smaller than that of copper at room temperature. It is called a **semiconductor,** because its electrical conductivity, although smaller than that of a metal, is far greater than that of an **insulator** such as diamond, which has a larger band gap. The conductivity of a semiconductor is increased by increasing the temperature, which excites more electrons into levels in the conduction band. Another way to increase the conductivity of a semiconductor is to irradiate it with a beam of electromagnetic radiation with a frequency high enough to excite electrons from the valence band to the conduction band. This process resembles the photoelectric effect described in Chapter 4, with the difference that now the electrons are not removed from the material but only moved into the conduction band, ready to conduct a current if a potential difference is imposed.

EXAMPLE 22.3

Calculate the longest wavelength of light that can excite electrons from the valence to the conduction band in silicon. In what region of the spectrum does this wavelength fall?

SOLUTION

The energy carried by a photon is $h\nu = hc/\lambda$, where h is Planck's constant, ν the photon frequency, c the speed of light, and λ the photon wavelength. For a photon to just excite an electron across the band gap, this energy must be equal to that band gap energy, $E_g = 1.94 \times 10^{-19}$ J, where

$$\frac{hc}{\lambda} = E_g$$

Solving for the wavelength gives

$$\begin{aligned}\lambda = \frac{hc}{E_g} &= \frac{(6.626 \times 10^{-34}\ \text{J s}) \times (2.998 \times 10^{8}\ \text{m s}^{-1})}{1.94 \times 10^{-19}\ \text{J}} \\ &= 1.02 \times 10^{-6}\ \text{m} = 1020\ \text{nm}\end{aligned}$$

This wavelength falls in the infrared region of the spectrum. Photons with shorter wavelengths (for example, visible light) carry more than enough energy to excite electrons to the conduction band in silicon.

Related Problems: 27, 28

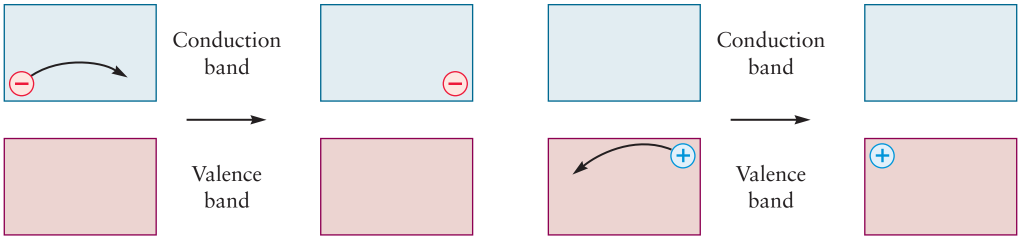
22.7 Semiconductors

Silicon in very high purity is said to display its **intrinsic properties**. When certain other elements are added to pure silicon in a process called **doping,** it acquires interesting electronic properties. For example, if atoms of a Group V element such as arsenic or antimony are diffused into silicon, they substitute for Si atoms in the network. Such atoms have five valence electrons, so each introduces one more electron into the silicon crystal than is needed for bonding. The extra electrons occupy energy levels just below the lowest level of the conduction band. Little energy is required to promote electrons from such a **donor impurity** level into the conduction band, and the electrical conductivity of the silicon crystal is increased without the necessity of increasing the temperature. Silicon doped with atoms of a Group V element is called an ***n*-type semiconductor** to indicate that the charge carrier is negative.

However, if a Group III element such as gallium is used as a dopant, there is one fewer electron in the valence band per dopant atom because Group III elements have only three valence electrons, not four. This situation corresponds to creating one **hole** in the valence band, with an effective charge of +1, for each Group III atom added. If a voltage difference is impressed across a crystal that is doped in this way, it causes the positively charged holes to move toward the negative source of potential. Equivalently, a valence band electron next to the (positive) hole will move in the opposite direction (that is, toward the positive source of potential). Whether we think of holes or electrons as the mobile charge carrier in the valence band, the result is the same; we are simply using different words to describe the same physical phenomenon (Fig. 22.22). Silicon that has been doped with a Group III element is called a ***p*-type semiconductor** to indicate that the carrier has an effective positive charge.

A different class of semiconductors is based not on silicon, but on equimolar compounds of Group III with Group V elements. Gallium arsenide, for example, is isoelectronic to the Group IV semiconductor germanium. When GaAs is doped with the Group VI element tellurium, an *n*-type semiconductor is produced; doping

FIGURE 22.22 (a) In an *n*-type semiconductor, a small number of electrons occupy levels in the conduction band. When an electric field is imposed, each electron moves (black arrows) into one of the numerous nearby vacant energy levels in the conduction band. (b) In a *p*-type semiconductor, a small number of levels in the valence band are unoccupied. Conduction occurs as electrons in the numerous occupied levels of the valence band jump into the sparsely distributed unoccupied levels. The arrow shows the motion of an electron to occupy a previously empty level. The process can also be described as the motion of positively charged holes in the opposite direction.



(a) Electron motion

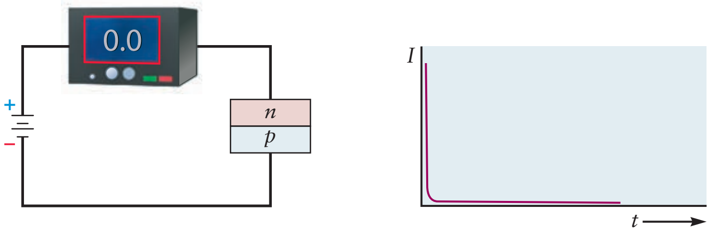
(b) "Hole" motion

with zinc, which has one *fewer* valence electron than gallium, gives a *p*-type semiconductor. Other III–V combinations have different band gaps and are useful in particular applications. Indium antimonide (InSb), for example, has a small enough band gap that absorption of infrared radiation causes electrons to be excited from the valence to the conduction band, and an electric current then flows when a small potential difference is applied. This compound is therefore used as a detector of infrared radiation. Still other compounds formed between the zinc group (zinc, cadmium, and mercury) and Group VI elements such as sulfur also have the same average number of valence electrons per atom as silicon and make useful semiconductors.

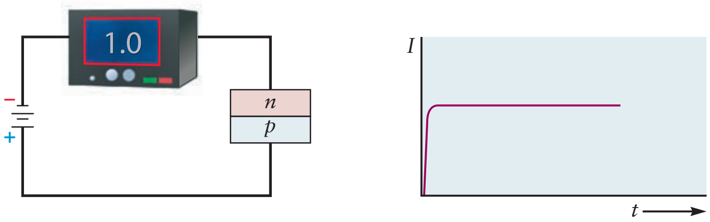
p–n Junctions and Device Performance

Of what value is it to have a semiconductor that can conduct an electric current by the flow of electrons if it is *n*-type or by the flow of holes if it is *p*-type? Many electronic functions can be fulfilled by semiconductors that possess these properties, but the simplest is **rectification**—the conversion of alternating current into

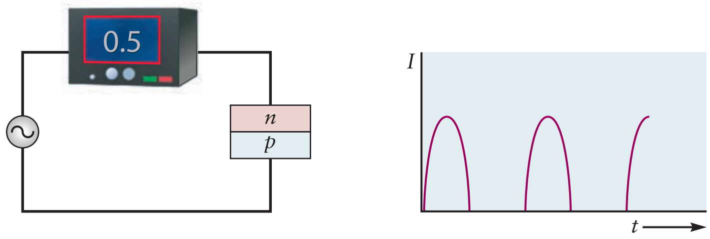
FIGURE 22.23 Current rectification by a *p–n* transistor.



(a) Current blocked



(b) Current flows



(c) Half-wave rectification of alternating current

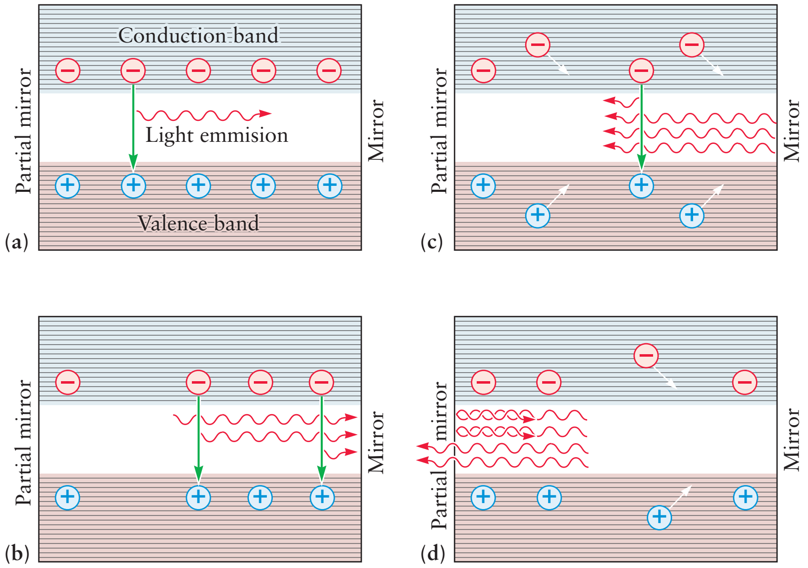


FIGURE 22.24 (a) In this solid-state laser, photons emitted as electrons and holes recombine to stimulate the emission of additional photons. (b) Reflection by a mirror on the right side sends coherent waves back through the laser medium. (c) Further amplification occurs by stimulated emission. (d) Some of the waves pass through a partially reflecting mirror on the left side.

direct current. Suppose thin crystals of *n*- and *p*-type silicon are placed in contact with one another and connected to a battery. In Figure 22.23a, the positive pole of the battery is connected to the *n*-type silicon, and the *p*-type silicon is connected to the negative pole. Only a small transient current can flow through the circuit in this case, because when the electrons in the conduction band of the *n*-type silicon have flowed out to the positive pole of the battery, there is none to take their place and current ceases to flow. However, if the negative pole of the battery is connected to the *n*-type silicon and the positive pole to the *p*-type silicon (see Fig. 22.23b), a steady current flows because electrons and holes move in opposite directions and recombine at the *n*–*p* junction. In effect, electrons flow toward the *n*–*p* junction in the *n*-type material, holes flow toward the *n*–*p* junction in the *p*-type material, and the junction is a “sink” where electrons fill the holes in the valence band and neutralize one another. If, instead of a galvanic cell, an alternating current source was connected to the *n*–*p* rectifier, current would flow in one direction only, creating pulsed direct current (see Fig. 22.23c).

Gallium arsenide and other semiconductors also provide materials for making solid-state lasers, which have applications ranging from reading compact discs to performing delicate eye surgery. When an electric current is passed through a material containing *n*–*p* junctions, electrons from the *n* regions and holes from the *p* regions flow toward the junctions, where they recombine and emit light. The light moves through the material, stimulating additional recombinations at other junctions and the emission of additional photons (Fig. 22.24). Critical to the operation of a laser is that these photons are coherent (in phase with one another), so the corresponding electric fields add constructively to create a plane wave. The light is reflected by a mirror at one end of the material and sets up a standing wave inside the semiconductor. At the other end, a partially reflecting mirror allows an intense beam of coherent light with a fixed wavelength to leave.

Semiconductors perform a wide range of electronic functions that formerly required the use of vacuum tubes. Vacuum tubes occupy much more space, generate large amounts of heat, and require considerably more energy to operate than **transistors,** their semiconductor counterparts. More important, semiconductors can be built into integrated circuits (Fig. 22.25) and made to store information and process it at great speeds.

Solar cells based on silicon or gallium arsenide provide a way to convert the radiant energy of the sun directly into electrical work by a technology that is virtually nonpolluting (Fig. 22.26). The high capital costs of solar cells make them uncompetitive with conventional fossil fuel sources of energy at this time, but as reserves of fossil fuels dwindle, solar energy will become an important option.

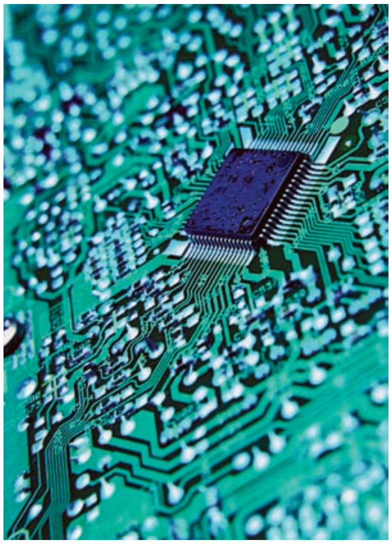

© Photodisc Red/Getty Images

FIGURE 22.25 An integrated circuit, like the microprocessor in a laptop computer, can contain hundreds of millions of transistors in a chip whose area is about 1 cm^2. The integrated circuit shown in this figure is connected to a printed circuit board by rows of wires on all four sides.

FIGURE 22.26 Silicon solar collectors are used on a large scale to harvest energy from the sun in this photovoltaic power plant located on one of the Tremiti Islands in Italy.
(© Tommaso Guicciardini/Science Photo Library/Photo Researchers, Inc.)

22.8 Pigments and Phosphors: Optical Displays

The band gap of an insulator or semiconductor has a significant effect on its color. Pure diamond has a large band gap, so even blue light does not have enough energy to excite electrons from the valence band to the conduction band. As a result, light passes through diamonds without being absorbed and the diamonds are colorless. Cadmium sulfide (CdS; Fig. 22.27) has a band gap of 4.2×10^{-19} J, which corresponds to a wavelength of 470 nm in the visible region of the spectrum. Cadmium sulfide, therefore, absorbs violet and blue light but strongly transmits yellow, giving it a deep yellow color. Cadmium sulfide is the pigment called cadmium yellow. Cinnabar (HgS, Fig. 22.28) has a smaller band gap of 3.2×10^{-19} J and absorbs all light except red. It has a deep red color and is the pigment vermilion. Semiconductors with band gaps of less than 2.8×10^{-19} J absorb all wavelengths of visible light and appear black. These include silicon (see Example 22.2), germanium, and gallium arsenide.

Doping silicon brings donor levels close enough to the conduction band or acceptor levels close enough to the valence band that thermal excitation can cause electrons to move into a conducting state. The corresponding doping of *insulators* or wide band-gap semiconductors can bring donor or acceptor states into positions where *visible light* can be absorbed or emitted. This changes the colors and optical properties of the materials. Nitrogen doped in diamond gives a donor impurity level in the band gap. Transitions to this level can absorb some blue light,

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FIGURE 22.27 Mixed crystals of two semiconductors with different band gaps, CdS (yellow) and CdSe (black), show a range of colors, illustrating a decrease in the band gap energy as the composition of the mixture becomes richer in Se.


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FIGURE 22.28 Crystalline cinnabar, HgS.

giving the diamond an undesirable yellowish color. In contrast, boron doped into diamond gives an acceptor level that absorbs red light most strongly and gives the highly prized and rare "blue diamond."

Phosphors are wide band-gap materials with dopants selected to create new levels such that particular colors of light are emitted. Electrons in these materials are excited by light of other wavelengths or by electrons hitting their surfaces, and light is then emitted as they return to lower energy states. A fluorescent lamp, for example, is a mercury-vapor lamp in which the inside of the tube has been coated with phosphors. The phosphors absorb the violet and ultraviolet light emitted by mercury vapor and emit at lower energies and longer wavelengths, giving a nearly white light that is more desirable than the bluish light that comes from a mercury-vapor lamp without the phosphors.

Phosphors are also used in television screens. The picture is formed by scanning a beam of electrons (from an electron gun) over the screen. The electrons strike the phosphors coating the screen, exciting their electrons and causing them to emit light. In a black-and-white television tube, the phosphors are a mixture of silver doped into ZnS, which gives blue light, and silver doped into $Zn_xCd_{1-x}S$, which gives yellow light. The combination of the two provides a reasonable approximation of white. A color television uses three different electron guns, with three corresponding types of phosphor on the screen. Silver doped in ZnS gives blue, manganese doped in Zn_2SiO_4 is used for green, and europium doped in YVO_4 gives red light. Masks are used to ensure that each electron beam encounters only the phosphors corresponding to the desired color.

CHAPTER SUMMARY

The properties of solid materials are determined by their microscopic structure, which in turn depends on the nature of the chemical bonds created during synthesis and processing. Mechanical and structural properties originate in strong ionic and covalent bonding. Electrical conductivity measures the movement of charged particles throughout the material. Metals, semiconductors, and insulators are distinguished by differences in conductivity values, as explained by the differences in their band gaps. In effect, this difference measures the extent to which some valence electrons from the atoms comprising the solid are delocalized while the remainder are involved in formation of localized bonds. Optical properties measure the response of the solid to visible light. The magnitude of the band gap determines what wavelength of light is absorbed, and therefore the color of the material.

CHAPTER REVIEW

- The mechanical properties of solid materials are determined by their internal structure, which in turn depends on the nature of the chemical bonds created during synthesis and processing.

    Silicate ceramics are well suited for structural applications because of their strength, which originates in the partially ionic, strong silicon–oxygen bonds in the tetrahedral orthosilicate anion. This structural unit appears in naturally occurring minerals and clays, which are fashioned into ceramic pieces through sintering and densification processes.

    Nonsilicate ceramics derive comparable properties from other inorganic structural units.

Oxide ceramics are made from oxides of numerous metals including beryllium, aluminum, calcium, and yttrium; these metal-oxide bonds are essentially ionic.

Nonoxide ceramics are based on the nitrogen and carbon compounds of silicon and boron. These compounds have short, strong, highly directional covalent bonds, so the materials have great structural strength but are brittle.

- The electrical properties measure the movement of charged particles in a material in response to an applied electric field. If the particles are free to move throughout the material, electrical conduction is the result, and the magnitude is measured by the electrical conductivity of the material.

Electrical conductivity depends on two separate microscopic parameters of a material: the number density of charge carriers present and the mobility of the carriers.

The band theory of solids explains the three broad classes of electronic conductivity seen in nature in terms of the number density of charge carriers available in classes of solids.

Metals have high conductivity values because the number density of free, mobile electrons is quite high—at least one per atom in the solid is in the conduction band. The "electron sea" is delocalized throughout the solid, and the free electrons respond easily to applied electric fields.

Insulating materials, such as the ceramics, have very low electrical conductivity because they have essentially no free electrons to carry current. There are no electrons in the conduction band, and the band gap is too large for electrons to be promoted from the valence band to the conduction band.

Semiconductors have conductivity values intermediate between metals and insulators because their bandgaps are small enough that electrons can be promoted from the valence band to the conduction band with modest thermal or optical excitation.

Doping a semiconductor by adding an electron donor impurity creates new states very near the bottom of the conduction band, so electrons can be promoted from the donor into the conduction band without increasing the temperature. These promoted electrons are now free to respond to an applied electric field. This doping process leads to an *n*-type semiconductor, in which the charge carrier is an electron.

Doping a semiconductor by adding an electron acceptor impurity creates new states very near the top of the valence band. An electron can move to this impurity state from the valence band, leaving a positively charged hole in the valence band. The hole can move in response to an applied electric field. This doping process leads to a *p*-type semiconductor, in which the charge carrier is a hole.

When a *p*-type semiconductor is placed in contact with an *n*-type semiconductor and the resulting *p*–*n* junction is placed in an electrical circuit, the junction can either pass or block DC current, or rectify AC current depending on details of the circuit. The device can emit light due to recombination of holes and electrons at the junction.

- Optical properties describe the response of a material to light in the visible range of the electromagnetic spectrum.

The bandgap of an insulator or semiconductor determines the wavelength of light absorbed by the material. Because the remaining portions of white light are transmitted through the material, color of the material is complementary to the wavelength of the light absorbed.

Many insulators are not colored because their bandgaps are so large that no visible light is absorbed. Adding dopants can introduce donor or acceptor states that enable absorption of visible light, so the doped materials are colored.

Phosphors are wide bandgap materials doped to emit light at specific wavelengths upon excitation by electron impact or incident light at other wavelengths. Phosphors are used to generate visible light in fluorescent fixtures, and to display signals on video monitors.

CONCEPTS & SKILLS

After studying this chapter and working the problems that follow, you should be able to:

1. Show how the fundamental silicate tetrahedral unit (SiO_4^{4-}) links to other silicate tetrahedra to form rings, chains, double chains, sheets, and space-filling crystalline networks (Section 22.1, Problems 1–4).
2. Describe the chemical compositions and structures of aluminosilicates, clays, and zeolites (Section 22.1, Problems 5–6).
3. Describe the structure of ceramic materials and the ways in which they are formed (Section 22.2).
4. Outline the properties of pottery, glass, and cement and the chemical reactions that give them structural strength (Section 22.3, Problems 7–14).
5. List several important oxide and mixed oxide ceramics and give some of their uses (Section 22.4, Problems 15–16).
6. Discuss the special properties of nonoxide ceramics and the kinetic and thermodynamic factors that make them useful (Section 22.4, Problems 17–20).
7. Explain how the conductivity of a material is measured and relate it to the number and mobility of charge carriers (Section 22.5, Problems 21–26).
8. Use the band model to describe the conductivity of metals, semiconductors, and insulators (Section 22.6, Problems 27–30).
9. Describe the mechanism of action of intrinsic, *n*-type, and *p*-type semiconductors (Section 22.7, Problems 31–34).
10. Describe how silicon-based solar energy collectors operate (Section 22.7).
11. Relate the band gap of a semiconductor or phosphor to the frequencies of electromagnetic radiation absorbed or emitted when electrons make transitions between the valence and conduction bands (Section 22.8, Problems 35–36).

KEY EQUATIONS

$$I = GV \qquad \text{(Section 22.5)}$$

$$R = \frac{\ell}{A}\rho \qquad \text{(Section 22.5)}$$

$$\sigma = \frac{1}{\rho} = \frac{\ell}{RA} \qquad \text{(Section 22.5)}$$

$$J = \sigma E \qquad \text{(Section 22.5)}$$

$$|\vec{v}_d| = \mu|\vec{E}| \qquad \text{(Section 22.5)}$$

$$\Lambda_m = |z|\mu\mathcal{F} \qquad \text{(Section 22.5)}$$

$$\sigma_{\text{ion}} = |z|en_{\text{ion}}\,\mu_{\text{ion}} \qquad \text{(Section 22.5)}$$

$$\sigma_{\text{tot}} = |z_{\text{cation}}|en_{\text{cation}}\,\mu_{\text{cation}} + |z_{\text{anion}}|en_{\text{anion}}\,\mu_{\text{anion}} \qquad \text{(Section 22.5)}$$

$$\sigma_{\text{el}} = en_{\text{el}}\,\mu_{\text{el}} \qquad \text{(Section 22.5)}$$

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G. Problems that are more challenging are indicated with asterisks.

Minerals: Naturally Occurring Inorganic Materials

1. Draw a Lewis electron-dot diagram for the disilicate ion ($Si_2O_7^{6-}$). What changes in this structure would be necessary to produce the structure of the pyrophosphate ion ($P_2O_7^{4-}$) and the pyrosulfate ion ($S_2O_7^{2-}$)? What is the analogous compound of chlorine?

2. Draw a Lewis electron-dot diagram for the cyclosilicate ion ($Si_6O_{18}^{12-}$), which forms part of the structures of beryl and emerald.

3. Using Table 22.1, predict the structure of each of the following silicate minerals (network, sheets, double chains, and so forth). Give the oxidation state of each atom.
- (a) Andradite, $Ca_3Fe_2(SiO_4)_3$
- (b) Vlasovite, $Na_2ZrSi_4O_{10}$
- (c) Hardystonite, $Ca_2ZnSi_2O_7$
- (d) Chrysotile, $Mg_3Si_2O_5(OH)_4$

4. Using Table 22.1, predict the structure of each of the following silicate minerals (network, sheets, double chains, and so forth). Give the oxidation state of each atom.
- (a) Tremolite, $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$
- (b) Gillespite, $BaFeSi_4O_{10}$
- (c) Uvarovite, $Ca_3Cr_2(SiO_4)_3$
- (d) Barysilate, $MnPb_8(Si_2O_7)_3$

5. Using Table 22.1, predict the structure of each of the following aluminosilicate minerals (network, sheets, double chains, and so forth). In each case, the Al atoms grouped with the Si and O in the formula substitute for Si in tetrahedral sites. Give the oxidation state of each atom.
- (a) Keatite, $Li(AlSi_2O_6)$
- (b) Muscovite, $KAl_2(AlSi_3O_{10})(OH)_2$
- (c) Cordierite, $Al_3Mg_2(AlSi_5O_{18})$

6. Using Table 22.1, predict the structure of each of the following aluminosilicate minerals (network, sheets, double chains, and so forth). In each case, the Al atoms grouped with the Si and O in the formula substitute for Si in tetrahedral sites. Give the oxidation state of each atom.
- (a) Amesite, $Mg_2Al(AlSiO_5)(OH)_4$
- (b) Phlogopite, $KMg_3(AlSi_3O_{10})(OH)_2$
- (c) Thomsonite, $NaCa_2(Al_5Si_5O_{20}) \cdot 6\ H_2O$

Silicate Ceramics

7. A ceramic that has been much used by artisans and craftsmen for the carving of small figurines is based on the mineral steatite (commonly known as soapstone). Steatite is a hydrated magnesium silicate that has the composition $Mg_3Si_4O_{10}(OH)_2$. It is remarkably soft—a fingernail can scratch it. When heated in a furnace to about 1000°C, chemical reaction transforms it into a hard, two-phase composite of magnesium silicate ($MgSiO_3$) and quartz in much the same way that clay minerals are converted into mullite ($Al_6Si_2O_{13}$) and cristobalite (SiO_2) on firing. Write a balanced chemical equation for this reaction.

8. A clay mineral that is frequently used together with or in place of kaolinite is pyrophyllite ($Al_2Si_4O_{10}(OH)_2$). Write a balanced chemical equation for the production of mullite and cristobalite on the firing of pyrophyllite.

9. Calculate the volume of carbon dioxide produced at standard temperature and pressure when a sheet of ordinary glass of mass 2.50 kg is made from its starting materials—sodium carbonate, calcium carbonate, and silica. Take the composition of the glass to be $Na_2O{\cdot}CaO{\cdot}(SiO_2)_6$.

10. Calculate the volume of steam produced when a 4.0-kg brick made from pure kaolinite is completely dehydrated at 600°C and a pressure of 1.00 atm.

11. A sample of soda-lime glass for tableware is analyzed and found to contain the following percentages by mass of oxides: SiO_2, 72.4%; Na_2O, 18.1%; CaO, 8.1%; Al_2O_3, 1.0%; MgO, 0.2%; BaO, 0.2%. (The elements are not actually present as binary oxides, but this is the way compositions are usually given.) Calculate the chemical amounts of Si, Na, Ca, Al, Mg, and Ba atoms per mole of O atoms in this sample.

12. A sample of Portland cement is analyzed and found to contain the following percentages by mass of oxides: CaO, 64.3%; SiO_2, 21.2%; Al_2O_3, 5.9%; Fe_2O_3, 2.9%; MgO, 2.5%; SO_3, 1.8%; Na_2O, 1.4%. Calculate the chemical amounts of Ca, Si, Al, Fe, Mg, S, and Na atoms per mole of O atoms in this sample.

13. The most important contributor to the strength of hardened Portland cement is tricalcium silicate, $(CaO)_3{\cdot}SiO_2$, for which the measured standard enthalpy of formation is -2929.2 kJ mol^{-1}. Calculate the standard enthalpy change for the production of 1.00 mol tricalcium silicate from quartz and lime.

14. One of the simplest of the heat-generating reactions that occur when water is added to cement is the production of calcium hydroxide (slaked lime) from lime. Write a balanced chemical equation for this reaction, and use data from Appendix D to calculate the amount of heat generated by the reaction of 1.00 kg lime with water at room conditions.

Nonsilicate Ceramics

15. Calculate the average oxidation number of the copper in $YBa_2Cu_3O_{9-x}$ if $x = 2$. Assume that the rare-earth element yttrium is in its usual +3 oxidation state.

16. The mixed oxide ceramic $Tl_2Ca_2Ba_2Cu_3O_{10+x}$ has zero electrical resistance at 125 K. Calculate the average oxidation number of the copper in this compound if $x = 0.50$ and thallium is in the +3 oxidation state.

17. Silicon carbide (SiC) is made by the high-temperature reaction of silica sand (quartz) with coke; the byproduct is carbon monoxide.
- (a) Write a balanced chemical equation for this reaction.
- (b) Calculate the standard enthalpy change per mole of SiC produced.
- (c) Predict (qualitatively) the following physical properties of silicon carbide: conductivity, melting point, and hardness.

18. Boron nitride (BN) is made by the reaction of boron trichloride with ammonia.
  - **(a)** Write a balanced chemical equation for this reaction.
  - **(b)** Calculate the standard enthalpy change per mole of BN produced, given that the standard molar enthalpy of formation of BN(s) is (254.4 kJ mol^{-1}.
  - **(c)** Predict (qualitatively) the following physical properties of boron nitride: conductivity, melting point, and hardness.

19. The standard free energy of formation of cubic silicon carbide (SiC) is (62.8 kJ mol^{-1}. Determine the standard free energy change when 1.00 mol SiC reacts with oxygen to form SiO_2 (s, quartz) and $CO_2(g)$. Is silicon carbide thermodynamically stable in the air at room conditions?

20. The standard free energy of formation of boron carbide (B_4C) is (71 kJ mol^{-1}. Determine the standard free energy change when 1.00 mol B_4C reacts with oxygen to form $B_2O_3(s)$ and $CO_2(g)$. Is boron carbide thermodynamically stable in the air at room conditions?

Electrical Conduction in Materials

21. A cylindrical sample of solid germanium has length 55.0 mm and diameter 5.0 mm. In a test circuit, 0.150 A of current flowed through this sample when the voltage applied between its ends was 17.5 V. What is the electrical conductivity of this sample?

22. A gold wire 4.0 mm in diameter and 1.5 m in length is to be used in a test circuit. (a) Calculate the resistance of the wire. (b) Calculate the current density in the wire when the voltage applied between its ends is 0.070 V. (c) Calculate the electric field in the wire.

23. The mobilities for Na^+ and Cl^- in aqueous solution are given in Table 22.7. Calculate the conductivity of a 0.10-M solution of NaCl in water at 25°C.

24. Explain why the ionic mobility of CH_3COO^- is smaller than that for Cl^-.

25. The electrical conductivity for copper is given in Table 22.6. The electron mobility in copper at room temperature is 3.0×10^{-3} m^2 V^{-1} s^{-1}. Using the Drude model for metallic conductivity, calculate the number of free electrons per Cu atom. The density of copper is 8.9 g cm^{-3}.

26. A variety of useful metallic alloys can be prepared by dissolving Ni in Cu. The room temperature resistivity of pure copper is 1.6×10^{-8} Ω m. As nickel is dissolved in copper up to 50% mass, the resistivity increases in a nearly linear fashion to the value 47.0×10^{-8} Ω m. Explain this increase qualitatively.

Band Theory of Conduction

27. Electrons in a semiconductor can be excited from the valence band to the conduction band through the absorption of photons with energies exceeding the band gap. At room temperature, indium phosphide (InP) is a semiconductor that absorbs light only at wavelengths less than 920 nm. Calculate the band gap in InP.

28. Both GaAs and CdS are semiconductors that are being studied for possible use in solar cells to generate electric current from sunlight. Their band gaps are 2.29×10^{-19} J and 3.88×10^{-19} J, respectively, at room temperature. Calculate the longest wavelength of light that is capable of exciting electrons across the band gap in each of these substances. In which region of the electromagnetic spectrum do these wavelengths fall? Use this result to explain why CdS-based sensors are used in some cameras to estimate the proper exposure conditions.

29. The number of electrons excited to the conduction band per cubic centimeter in a semiconductor can be estimated from the following equation:

$$n_e = (4.8 \times 10^{15}\ \text{cm}^{-3}\ \text{K}^{-3/2})\ T^{3/2}\ e^{-E_g/(2RT)}$$

where T is the temperature in kelvins and E_g the band gap in joules *per mole*. The band gap of diamond at 300 K is 8.7×10^{-19} J. How many electrons are thermally excited to the conduction band at this temperature in a 1.00-cm^3 diamond crystal?

30. The band gap of pure crystalline germanium is 1.1×10^{-19} J at 300 K. How many electrons are excited from the valence band to the conduction band in a 1.00-cm^3 crystal of germanium at 300 K? Use the equation given in the preceding problem.

Semiconductors

31. Describe the nature of electrical conduction in (a) silicon doped with phosphorus and (b) indium antimonide doped with zinc.

32. Describe the nature of electrical conduction in (a) germanium doped with indium and (b) cadmium sulfide doped with arsenic.

33. In a light-emitting diode (LED), which is used in displays on electronic equipment, watches, and clocks, a voltage is imposed across an n–p semiconductor junction. The electrons on the n side combine with the holes on the p side and emit light at the frequency of the band gap. This process can also be described as the emission of light as electrons fall from levels in the conduction band to empty levels in the valence band. It is the reverse of the production of electric current by illumination of a semiconductor.

Many LEDs are made from semiconductors that have the general composition $GaAs_{1-x}P_x$. When x is varied between 0 and 1, the band gap changes and, with it, the color of light emitted by the diode. When $x = 0.4$, the band gap is 2.9×10^{-19} J. Determine the wavelength and color of the light emitted by this LED.

34. When the LED described in Problem 33 has the composition $GaAs_{0.14}P_{0.86}$ (i.e., $x = 0.86$), the band gap has increased to 3.4×10^{-19} J. Determine the wavelength and color of the light emitted by this LED.

Pigments and Phosphors: Optical Displays

35. The pigment zinc white (ZnO) turns bright yellow when heated, but the white color returns when the sample is cooled. Does the band gap increase or decrease when the sample is heated?

36. Mercury(II) sulfide (HgS) exists in two different crystalline forms. In cinnabar, the band gap is 3.2×10^{-19} J; in metacinnabar, it is 2.6×10^{-19} J. In some old paintings with improperly formulated paints, the pigment vermilion (cinnabar) has transformed to metacinnabar on exposure to light. Describe the color change that results.

ADDITIONAL PROBLEMS

37. Predict the structure of each of the following silicate minerals (network, sheets, double chains, and so forth). Give the oxidation state of each atom.
    (a) Apophyllite, $KCa_4(Si_8O_{20})F \cdot 8\ H_2O$
    (b) Rhodonite, $CaMn_4(Si_5O_{15})$
    (c) Margarite, $CaAl_2(Al_2Si_2O_{10})(OH)_2$

38. Using Table 22.1, predict the kind of structure formed by manganpyrosmalite, a silicate mineral with chemical formula $Mn_{12}FeMg_3(Si_{12}O_{30})(OH)_{10}Cl_{10}$. Give the oxidation state of each atom in this formula unit.

39. A reference book lists the chemical formula of one form of vermiculite as

$$[(Mg_{2.36}Fe_{0.48}Al_{0.16})(Si_{2.72}Al_{1.28})O_{10}(OH)_2][Mg_{0.32}(H_2O)_{4.32}]$$

Determine the oxidation state of the iron in this mineral.

40. The most common feldspars are those that contain potassium, sodium, and calcium cations. They are called, respectively, orthoclase ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$), and anorthite ($CaAl_2Si_2O_8$). The solid solubility of orthoclase in albite is limited, and its solubility in anorthite is almost negligible. Albite and anorthite, however, are completely miscible at high temperatures and show complete solid solution. Offer an explanation for these observations, based on the tabulated radii of the K^+, Na^+, and Ca^{2+} ions from Appendix F.

41. The clay mineral kaolinite ($Al_2Si_2O_5(OH)_4$) is formed by the weathering action of water containing dissolved carbon dioxide on the feldspar mineral anorthite ($CaAl_2Si_2O_8$). Write a balanced chemical equation for the reaction that occurs. The CO_2 forms H_2CO_3 as it dissolves. As the pH is lowered, will the weathering occur to a greater or a lesser extent?

42. Certain kinds of zeolite have the general formula $M_2O{\cdot}Al_2O_3{\cdot}ySiO_2{\cdot}wH_2O$, where M is an alkali metal such as sodium or potassium, y is 2 or more, and w is any integer. Compute the mass percentage of aluminum in a zeolite that has $M = K$, $y = 4$, and $w = 6$.

43. (a) Use data from Tables 15.2 and 16.2 to calculate the solubility of $CaCO_3$ in water at pH 7.
    (b) Will the solubility increase or decrease if the pH is lowered and the water becomes more acidic?
    (c) Calculate the maximum amount of limestone (primarily calcium carbonate) that could dissolve per year in a river at pH 7 with an average flow rate of $1.0 \times 10^6\ m^3/h$.

* 44. Silica (SiO_2) exists in several forms, including quartz (molar volume $22.69\ cm^3\ mol^{-1}$) and cristobalite (molar volume $25.74\ cm^3\ mol^{-1}$).
    (a) Use data from Appendix D to calculate $\Delta H°$, $\Delta S°$, and ΔG at 25°C.
    (b) Which form is thermodynamically stable at 25°C?
    (c) Which form is stable at very high temperatures, provided that melting does not occur first?

45. Talc, $Mg_3Si_4O_{10}(OH)_2$, reacts with forsterite (Mg_2SiO_4) to form enstatite ($MgSiO_3$) and water vapor.
    (a) Write a balanced chemical equation for this reaction.
    (b) If the water pressure is equal to the total pressure, will formation of products be favored or disfavored with increasing total pressure?
    (c) The entropy change for this reaction is positive. Will the slope of the coexistence curve (pressure plotted against temperature) be positive or negative?

46. In what ways does soda-lime glass resemble and in what ways does it differ from a pot made from the firing of kaolinite? Include the following aspects in your discussion: composition, structure, physical properties, and method of preparation.

47. Iron oxides are red when the average oxidation state of iron is high and black when it is low. To impart each of these colors to a pot made from clay that contains iron oxides, would you use an air-rich or a smoky atmosphere in the kiln? Explain.

48. Refractories can be classified as acidic or basic, depending on the properties of the oxides in question. A basic refractory must not be used in contact with acid, and an acidic refractory must not be used in contact with a base. Classify magnesia and silica as acidic or basic refractories.

49. Dolomite bricks are used in the linings of furnaces in the cement and steel industries. Pure dolomite contains 45.7% $MgCO_3$ and 54.3% $CaCO_3$ by mass. Determine the empirical formula of dolomite.

50. Beryllia (BeO) ceramics have some use but show only poor resistance to strong acids and bases. Write likely chemical equations for the reaction of BeO with a strong acid and with a strong base.

51. Silicon nitride resists all acids except hydrofluoric, with which it reacts to give silicon tetrafluoride and ammonia. Write a balanced chemical equation for this reaction.

52. Compare oxide ceramics such as alumina (Al_2O_3) and magnesia (MgO), which have significant ionic character, with covalently bonded nonoxide ceramics such as silicon carbide (SiC) and boron carbide (B_4C; see Problems 19 and 20) with respect to thermodynamic stability at ordinary conditions.

53. Compare the hybridization of Si atoms in Si(s) with that of C atoms in graphite (see Fig. 21.26). If silicon were to adopt the graphite structure, would its electrical conductivity be high or low?

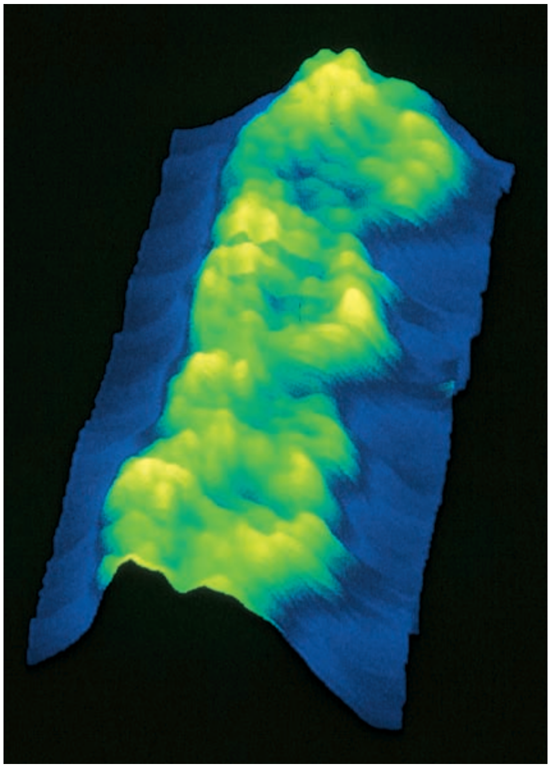
54. Describe how the band gap varies from a metal to a semiconductor to an insulator.

55. Suppose some people are sitting in a row at a movie theater, with a single empty seat on the left end of the row. Every 5 minutes, a person moves into a seat on his or her left if it is empty. In what direction and with what speed does the empty seat "move" along the row? Comment on the connection with hole motion in p-type semiconductors.

56. A sample of silicon doped with antimony is an n-type semiconductor. Suppose a small amount of gallium is added to such a semiconductor. Describe how the conduction properties of the solid will vary with the amount of gallium added.

CHAPTER 23

Polymeric Materials and Soft Condensed Matter



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A false-color scanning tunneling micrograph (STM) of a DNA double-helix molecule adsorbed on a graphite substrate.

The organic compounds discussed in Chapter 7 were relatively small molecules, ranging from four or five atoms (such as methane or formaldehyde) to long-chain hydrocarbons up to 30 carbon atoms with relative molecular masses of several hundred. In addition to these smaller molecules, carbon atoms string together in stable chains of essentially unlimited length. Such chains provide the backbones of truly huge molecules that may contain hundreds of thousands or even millions of atoms. Such compounds, called **polymers,** are formed by linking numerous separate small **monomer units** in strands and webs.

Although many polymers are based on the ability of carbon to form stable long-chain molecules with various functional groups attached, carbon is not unique in this ability. Recall from Chapter 22 the chains, sheets, and networks found in natural silicates, in which the elements silicon and oxygen join together to form extended structures. This chapter focuses on organic polymers, whose chemical and physical properties depend on the bonding and functional group chemistry discussed in Section 7.6. We examine both synthetic polymers, which are built largely from the hydrocarbon raw materials discussed in Section 7.1, and naturally occurring biopolymers such as starch, proteins, and nucleic acids, which are built from products of biological synthesis.

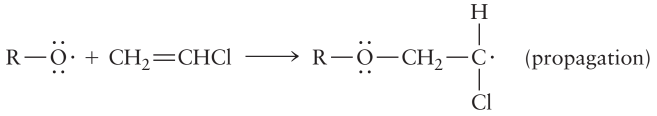
23.1 Polymerization Reactions for Synthetic Polymers

To construct a polymer, very many monomers must add to a growing polymer molecule, and the reaction must not falter after the first few molecules have reacted. This is achieved by having the polymer molecule retain highly reactive functional groups at all times during its synthesis. The two major types of polymer growth are addition polymerization and condensation polymerization.

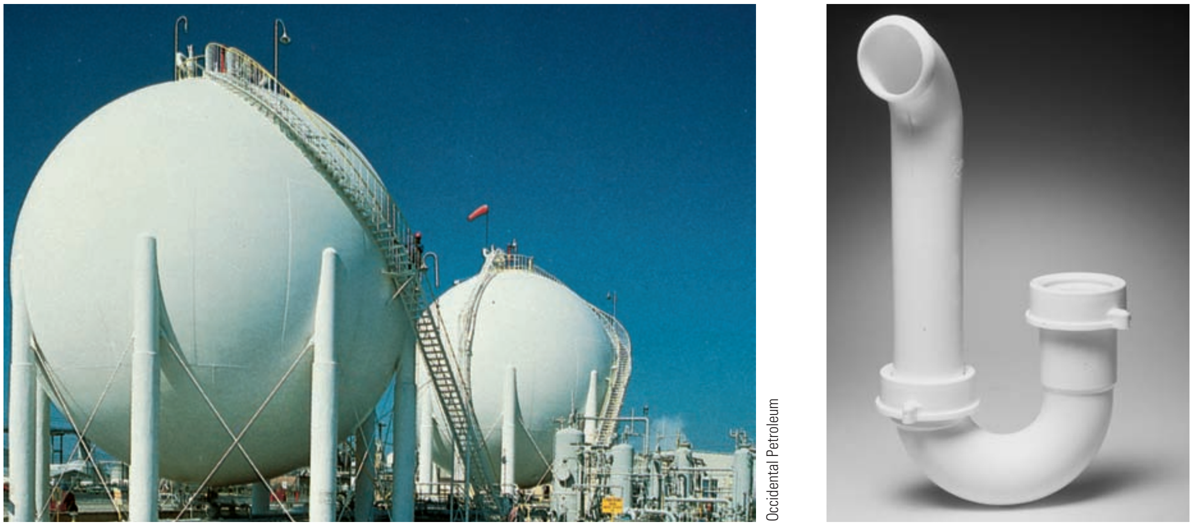
In **addition polymerization,** monomers react to form a polymer chain without net loss of atoms. The most common type of addition polymerization involves the free-radical chain reaction of molecules that have C=C bonds. As in the chain reactions considered in Section 18.4, the overall process consists of three steps: initiation, propagation (repeated many times to build up a long chain), and termination. As an example, consider the polymerization of vinyl chloride (chloroethene, $CH_2{=}CHCl$) to polyvinyl chloride (Fig. 23.1). This process can be initiated by a small concentration of molecules that have bonds weak enough to be broken by the action of light or heat, giving radicals. An example of such an **initiator** is a peroxide, which can be represented as R—O—O—R′, where R and R′ represent alkyl groups. The weak O—O bonds break

$$\mathrm{R{-}\ddot{\underset{\cdot\cdot}{O}}{-}\ddot{\underset{\cdot\cdot}{O}}{-}R' \longrightarrow R{-}\ddot{\underset{\cdot\cdot}{O}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{O}}{-}R'}\quad\text{(initiation)}$$

to give radicals, whose oxygen valence shells are incomplete. The radicals remedy this by reacting readily with vinyl chloride, accepting electrons from the C=C bonds to reestablish a closed-shell electron configuration on the oxygen atoms:



$$\mathrm{R{-}\ddot{\underset{\cdot\cdot}{O}}\cdot + CH_2{=}CHCl \longrightarrow R{-}\ddot{\underset{\cdot\cdot}{O}}{-}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}\cdot}\quad\text{(propagation)}$$


Occidental Petroleum

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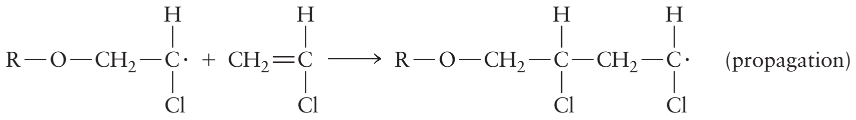
(a) (b)

FIGURE 23.1 (a) This chemical plant in Texas produces several billion kilograms of polyvinyl chloride each year. The spherical tanks store gaseous raw material. (b) A pipefitting of polyvinyl chloride.

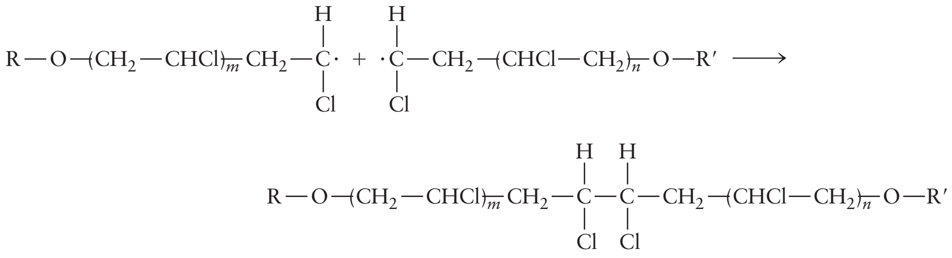
One of the two π electrons in the vinyl chloride double bond has been used to form a single bond with the $R-O\cdot$ radical. The other remains on the second carbon atom, leaving it as a seven–valence-electron atom that will react with another vinyl chloride molecule:



$$R-O-CH_2-\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}\cdot + CH_2=\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}} \longrightarrow R-O-CH_2-\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}-CH_2-\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}\cdot \qquad \text{(propagation)}$$

At each stage, the end group of the lengthening chain is one electron short of a valence octet and remains quite reactive. The reaction can continue, building up long-chain molecules of high molecular mass. The vinyl chloride monomers always attach to the growing chain with their CH_2 group because the odd electron is more stable on a CHCl end group. This gives the polymer a regular alternation of $-CH_2-$ and $-CHCl-$ groups. Its chemical formula is $(-CH_2CHCl-)_n$.

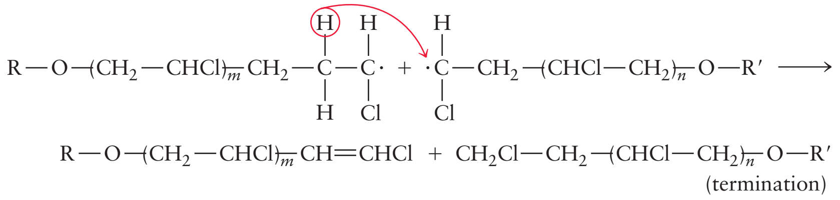
Termination occurs when the radical end groups on two different chains encounter each other and the two chains couple to give a longer chain:



$$R-O-(CH_2-CHCl)_m CH_2-\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}\cdot + \cdot\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}-CH_2-(CHCl-CH_2)_n-O-R' \longrightarrow$$

$$R-O-(CH_2-CHCl)_m CH_2-\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}-\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}-CH_2-(CHCl-CH_2)_n-O-R'$$

Alternatively, a hydrogen atom may transfer from one end group to the other:



$$R-O-(CH_2-CHCl)_m CH_2-\overset{\displaystyle \boxed{H}}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}\cdot + \cdot\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}-CH_2-(CHCl-CH_2)_n-O-R' \longrightarrow$$

$$R-O-(CH_2-CHCl)_m CH=CHCl + CH_2Cl-CH_2-(CHCl-CH_2)_n-O-R' \qquad \text{(termination)}$$

The latter termination step leaves a double bond on one chain end and a $-CH_2Cl$ group on the other. When the polymer molecules are long, the exact natures of the end groups have little effect on the physical and chemical properties of the material. A different type of hydrogen transfer step often has a much greater effect on the properties of the resulting polymer. Suppose that a hydrogen atom transfers not from the monomer unit on the *end* of a second chain but from a monomer unit in the middle of that chain (Fig. 23.2). Then the first chain stops growing, but

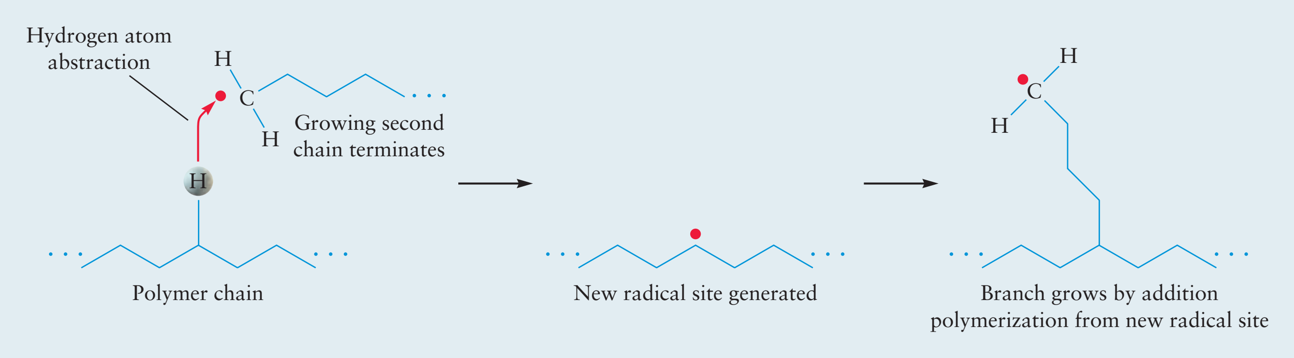
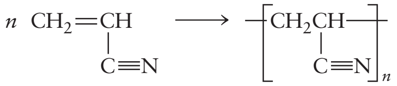


FIGURE 23.2 Chain branching can occur when a hydrogen atom is transferred (abstracted) from the middle of one chain to the free radical end of a second chain, thus terminating the growth of the second chain. The newly generated free radical in the middle of the polymer chain provides a site for the growth of a branched chain via continued monomer addition polymerization.

the radical site moves to the middle of the second chain, and growth resumes from that point, forming a *branched* polymeric chain with very different properties.

Addition polymerization can be initiated by ions as well as by free radicals. An example is the polymerization of acrylonitrile:



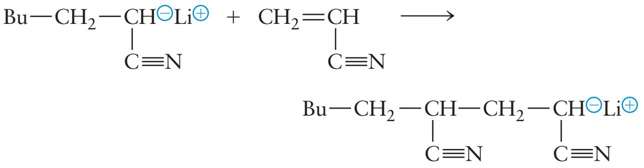
$$n\ CH_2{=}\underset{\substack{|\\ C\equiv N}}{CH} \longrightarrow \Big[CH_2\underset{\substack{|\\ C\equiv N}}{CH}\Big]_n$$

A suitable initiator for this process is butyl lithium, $(CH_3CH_2CH_2CH_2)^-Li^+$. The butyl anion (abbreviated Bu^-) reacts with the end carbon atom in a molecule of acrylonitrile to give a new anion:

$$Bu^{\ominus}Li^{\oplus} + CH_2{=}\underset{\substack{|\\ C\equiv N}}{CH} \longrightarrow Bu{-}CH_2{-}\underset{\substack{|\\ C\equiv N}}{CH}{}^{\ominus}Li^{\oplus}$$

(initiation)

The new anion then reacts with an additional molecule of acrylonitrile:

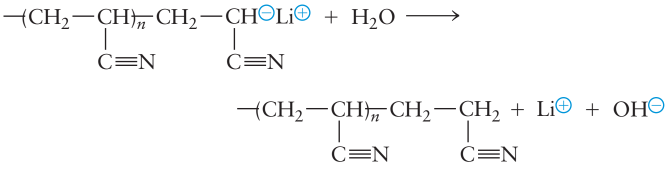


$$Bu{-}CH_2{-}\underset{\substack{|\\ C\equiv N}}{CH}{}^{\ominus}Li^{\oplus} + CH_2{=}\underset{\substack{|\\ C\equiv N}}{CH} \longrightarrow Bu{-}CH_2{-}\underset{\substack{|\\ C\equiv N}}{CH}{-}CH_2{-}\underset{\substack{|\\ C\equiv N}}{CH}{}^{\ominus}Li^{\oplus}$$

(propagation)

The process continues, building up a long-chain polymer.

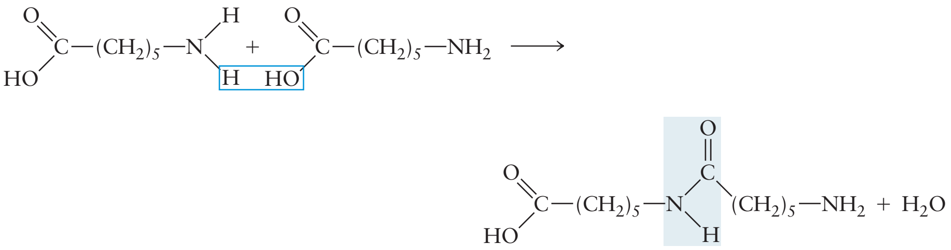
Ionic polymerization differs from free-radical polymerization because the negatively charged end groups repel one another, ruling out termination by the coupling of two chains. The ionic group at the end of the growing polymer is stable at each stage. Once the supply of monomer has been used up, the polymer can exist indefinitely with its ionic end group, in contrast with the free-radical case, in which some reaction must take place to terminate the process. Ion-initiated polymers are called "living" polymers because, when additional monomer is added (even months later), they resume growth and increase in molecular mass. Termination can be achieved by adding water to replace the Li^+ with a hydrogen ion:



$$-\!\!(CH_2{-}\underset{\substack{|\\ C\equiv N}}{CH})_n\!\!-CH_2{-}\underset{\substack{|\\ C\equiv N}}{CH}{}^{\ominus}Li^{\oplus} + H_2O \longrightarrow -\!\!(CH_2{-}\underset{\substack{|\\ C\equiv N}}{CH})_n\!\!-CH_2{-}\underset{\substack{|\\ C\equiv N}}{CH_2} + Li^{\oplus} + OH^{\ominus}$$

(termination)

A second important mechanism of polymerization is **condensation polymerization,** in which a small molecule (frequently water) is split off as each monomer unit is attached to the growing polymer.[1] An example is the polymerization of 6-aminohexanoic acid. The first two molecules react upon heating according to



An amide linkage and water form from the reaction of an amine with a carboxylic acid. The new molecule still has an amine group on one end and a carboxylic

---

[1] Condensation reactions have appeared several times outside the context of polymer synthesis. For example, two molecules of H_2SO_4 condense to form disulfuric acid ($H_2S_2O_7$), and a carboxylic acid condenses with an alcohol to form an ester (see Section 7.6).

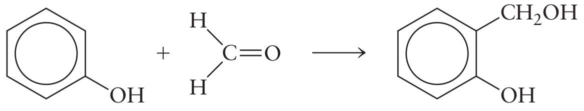
acid group on the other; it can therefore react with two more molecules of 6-aminohexanoic acid. The process repeats to build up a long-chain molecule. For each monomer unit added, one molecule of water is split off. The final polymer in this case is called nylon 6 and is used in fiber-belted radial tires and in carpets.

Both addition and condensation polymerization can be carried out with mixtures of two or more types of monomers present in the reaction mixture. The result is a **random copolymer** that incorporates both types of monomers in an irregular sequence along the chain. For example, a 1:6 molar ratio of styrene to butadiene monomers is used to make styrene–butadiene rubber (SBR) for automobile tires, and a 2:1 ratio gives a copolymer that is an ingredient in latex paints.

Cross-Linking: Nonlinear Synthetic Polymers

If every monomer forming a polymer has only two reactive sites, then only chains and rings can be made. The 6-aminohexanoic acid used in making nylon 6 has one amine group and one carboxylic acid group per molecule. When both functional groups react, one link is forged in the polymer chain, but that link cannot react further. If some or all of the monomers in a polymer have three or more reactive sites, however, then cross-linking to form sheets or networks is possible.

One important example of cross-linking involves phenol–formaldehyde copolymers (Fig. 23.3). When these two compounds are mixed (with the phenol in excess in the presence of an acid catalyst), straight-chain polymers form. The first step is the addition of formaldehyde to phenol to give methylolphenol:



Molecules of methylolphenol then undergo condensation reactions (releasing water) to form a linear polymer called novalac:

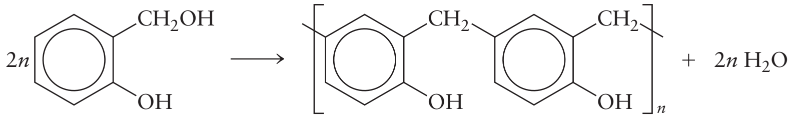


FIGURE 23.3 When a mixture of phenol (C_6H_5OH) and formaldehyde (CH_2O) dissolved in acetic acid is treated with concentrated hydrochloric acid, a phenol–formaldehyde polymer grows.

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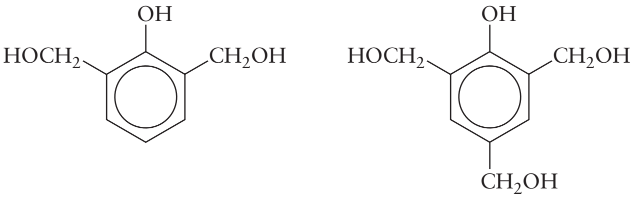
If, on the other hand, the reaction is carried out with an excess of formaldehyde, dimethylolphenols and trimethylolphenols form:



Each of these monomers has more than two reactive sites and can react with up to three others to form a cross-linked polymer that is much stronger and more impact-resistant than the linear polymer. The very first synthetic plastic, Bakelite, was made in 1907 from cross-linked phenol and formaldehyde. Modern phenol–formaldehyde polymers are used as adhesives for plywood; more than a billion kilograms are produced per year in the United States.

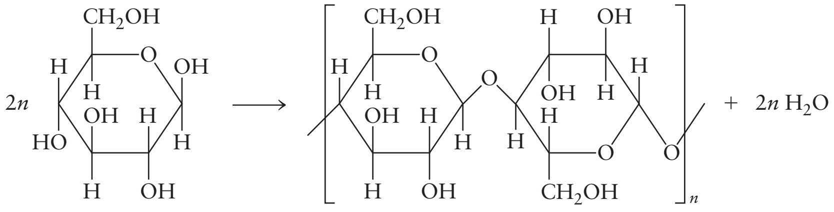
Cross-linking is often desirable because it leads to a stronger material. Sometimes cross-linking agents are added deliberately to form additional bonds between polymer chains. Polybutadiene contains double bonds that can be linked upon addition of appropriate oxidizing agents. One especially important kind of cross-linking occurs through sulfur chains in rubber, as we will see.

23.2 Applications for Synthetic Polymers

The three largest uses for polymers are in fibers, plastics, and elastomers (rubbers). We can distinguish between these three types of materials on the basis of their physical properties, especially their resistance to stretching. A typical fiber strongly resists stretching and can be elongated by less than 10% before breaking. Plastics are intermediate in their resistance to stretching and elongate 20% to 100% before breaking. Finally, elastomers stretch readily, with elongations of 100% to 1000% (that is, some types of rubber can be stretched by a factor of 10 without breaking). A fourth important class is the more recently developed electrically conducting polymers, which combine the optical and electronic properties of inorganic semiconductors with the processibility of conventional polymers. This section examines the major kinds of synthetic polymers and their uses.

Fibers

Many important fibers, including cotton and wool, are naturally occurring polymers. The first commercially successful synthetic polymers were made not by polymerization reactions but through the chemical regeneration of the natural polymer cellulose, a condensation polymer of the sugar glucose that is made by plants:



In the viscose rayon process, still used today, cellulose is digested in a concentrated solution of NaOH to convert the —OH groups to $-O^- \; Na^+$ ionic groups. Reac-

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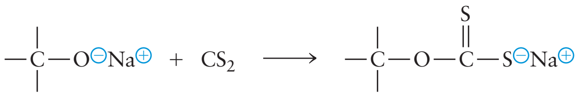
FIGURE 23.4 Filter paper (cellulose) will dissolve in a concentrated ammonia solution containing $[Cu(NH_3)_4]^{2+}$ ions. When the solution is extruded into aqueous sulfuric acid, a dark blue thread of rayon (regenerated cellulose) precipitates.

tion with CS_2 leads to the formation of about one "xanthate" group for every two glucose monomer units:

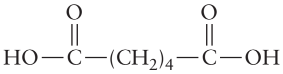


$$-\overset{|}{\underset{|}{C}}-O^{\ominus}Na^{\oplus} + CS_2 \longrightarrow -\overset{|}{\underset{|}{C}}-O-\overset{\overset{S}{\|}}{C}-S^{\ominus}Na^{\oplus}$$

Xanthate

Such substitutions reduce the hydrogen-bond forces holding polymer chains together. In the ripening step, some of these xanthate groups are removed with regeneration of CS_2, and others migrate to the $-CH_2OH$ groups from the ring $-OH$ groups. Afterward, sulfuric acid is added to neutralize the NaOH and to remove the remaining xanthate groups. At the same time, the viscose rayon is spun out to form fibers (Fig. 23.4) while new hydrogen bonds form.

Rayon is a "semisynthetic" fiber because it is prepared from a natural polymeric starting material. The first truly synthetic polymeric fiber was nylon, developed in the 1930s by the American chemist Wallace Carothers at DuPont Company. He knew of the condensation of an amine with a carboxylic acid to form an amide linkage (see Section 7.6) and noted that, if each molecule had *two* amine or carboxylic acid functional groups, long-chain polymers could form. The specific starting materials upon which Carothers settled, after numerous attempts, were adipic acid and hexamethylenediamine:



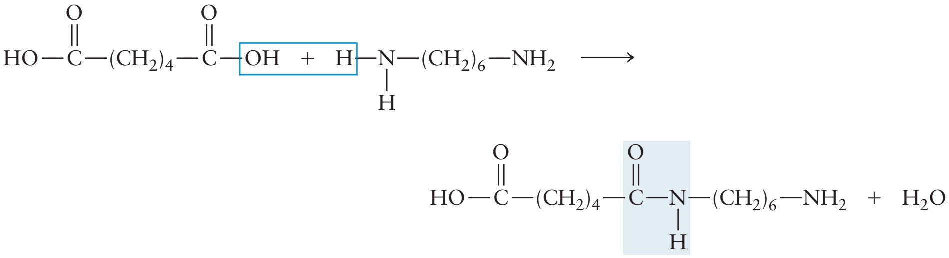
$$HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-OH$$

Adipic acid

$$H_2N-(CH_2)_6-NH_2$$

Hexamethylenediamine

The two react with loss of water, according to the equation



$$HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\boxed{OH + H}-\underset{\underset{H}{|}}{N}-(CH_2)_6-NH_2 \longrightarrow$$

$$HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-(CH_2)_6-NH_2 + H_2O$$

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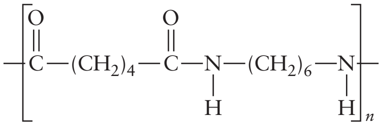
FIGURE 23.5 Hexamethylenediamine is dissolved in water (lower layer), and adipyl chloride, a derivative of adipic acid, is dissolved in hexane (upper layer). At the interface between the layers, nylon forms and is drawn out onto the stirring bar.

The resulting molecule has a carboxylic acid group on one end (which can react with another molecule of hexamethylenediamine) and an amine group on the other end (which can react with another molecule of adipic acid). The process can continue indefinitely, leading to a polymer with the formula

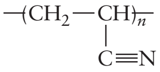


$$\left[-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-(CH_2)_6-\underset{\underset{H}{|}}{N}-\right]_n$$

called nylon 66 (Fig. 23.5). The nylon is extruded as a thread or spun as a fiber from the melt. The combination of well-aligned polymer molecules and $N-H\cdots O$ hydrogen bonds between chains makes nylon one of the strongest materials known. The designation "66" indicates that this nylon has six carbon atoms on the starting carboxylic acid and six on the diamine. Other nylons can be made with different numbers of carbon atoms.

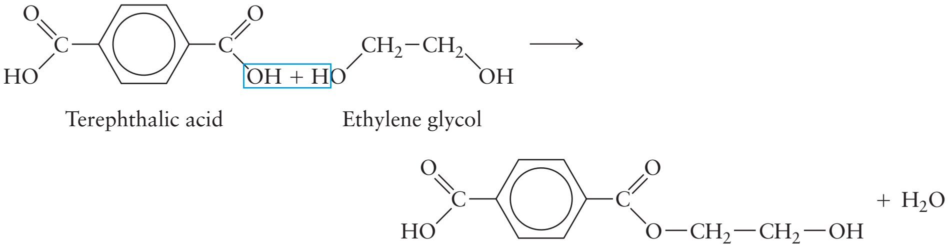
Just as a carboxylic acid reacts with an amine to give an amide, it also reacts with an alcohol to give an ester. This suggests the possible reaction of a dicarboxylic acid and a glycol (dialcohol) to form a polymer. The polymer produced most extensively in this way is polyethylene terephthalate, which is built up from

TABLE 23.1 Fibers

Name	Structural Units	Properties	Sample Uses
Rayon	Regenerated cellulose	Absorbent, soft, easy to dye, poor wash and wear	Dresses, suits, coats, curtains, blankets
Acetate	Acetylated cellulose	Fast drying, supple, shrink-resistant	Dresses, shirts, draperies, upholstery
Nylon	Polyamide	Strong, lustrous, easy to wash, smooth, resilient	Carpeting, upholstery, tents, sails, hosiery, stretch fabrics, rope
Dacron	Polyester	Strong, easy to dye, shrink-resistant	Permanent-press fabrics, rope, sails, thread
Acrylic (Orlon)	 $-\!\!(CH_2-\underset{\substack{\vert\\ C\equiv N}}{CH})_{\overline{n}}$	Warm, lightweight, resilient, quick-drying	Carpeting, sweaters, baby clothes, socks

Adapted from P. J. Chenier, *Survey of Industrial Chemistry.* New York: John Wiley & Sons, 1986, Table 18.4.

terephthalic acid (a benzene ring with $-COOH$ groups on both ends) and ethylene glycol. The first two molecules react according to



Further reaction then builds up the polymer, which is called polyester and sold under trade names such as Dacron. The planar benzene rings in this polymer make it stiffer than nylon, which has no aromatic groups in its backbone, and help make polyester fabrics crush-resistant. The same polymer formed in a thin sheet rather than a fiber becomes Mylar, a very strong film used for audio and video tapes.

Table 23.1 summarizes the structures, properties, and uses of some important fibers.

Plastics

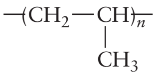
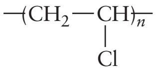
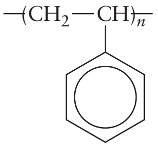
Plastics are loosely defined as polymeric materials that can be molded or extruded into desired shapes and that harden upon cooling or solvent evaporation. Rather than being spun into threads in which their molecules are aligned, as in fibers, plastics are cast into three-dimensional forms or spread into films for packaging applications. Although celluloid articles were fabricated by plastic processing by the late 1800s, the first important synthetic plastic was Bakelite, the phenol–formaldehyde resin whose cross-linking was discussed earlier in this section. Table 23.2 lists some of the most important plastics and their properties.

Ethylene ($CH_2{=}CH_2$) is the simplest monomer that will polymerize. Through free-radical–initiated addition polymerization at high pressures (1000 atm to 3000 atm) and temperatures (300°C to 500°C), it forms polyethylene:

$$n\ CH_2{=}CH_2 \longrightarrow +\!CH_2OCH_2\!+_n$$

The polyethylene formed in this way is not the perfect linear chain implied by this simple equation. Free radicals frequently abstract hydrogen from the middles of chains in this synthesis, so the polyethylene is heavily branched with hydrocarbon side chains of varying length. It is called **low-density polyethylene** (LDPE) because the difficulty of packing the irregular side chains gives it a lower density (<0.94 g

TABLE 23.2 Plastics

Name	Structural Units	Properties	Sample Uses
Polyethylene	$\left(CH_2-CH_2\right)_n$	High density: hard, strong, stiff	Molded containers, lids, toys, pipe
		Low density: soft, flexible, clear	Packaging, trash bags, squeeze bottles
Polypropylene	 $\left(CH_2-\underset{CH_3}{\underset{\mid}{CH}}\right)_n$	Stiffer, harder than high-density polyethylene, higher melting point	Containers, lids, carpeting, luggage, rope
Polyvinyl chloride	 $\left(CH_2-\underset{Cl}{\underset{\mid}{CH}}\right)_n$	Nonflammable, resistant to chemicals	Water pipes, roofing, credit cards, records
Polystyrene		Brittle, flammable, not resistant to chemicals, easy to process and dye	Furniture, toys, refrigerator linings, insulation
Phenolics	Phenol–formaldehyde copolymer	Resistant to heat, water, chemicals	Plywood adhesive, Fiberglass binder, circuit boards

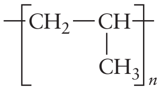
Adapted from P. J. Chenier, *Survey of Industrial Chemistry.* New York: John Wiley & Sons, 1986, pp. 252–264.

cm^{-3}) than that of perfectly linear polyethylene. This irregularity also makes it relatively soft, so its primary uses are in coatings, plastic packaging, trash bags, and squeeze bottles in which softness is an advantage, not a drawback.

A major breakthrough occurred in 1954, when the German chemist Karl Ziegler showed that ethylene could also be polymerized with a catalyst consisting of $TiCl_4$ and an organoaluminum compound [for example, $Al(C_2H_5)_3$]. The addition of ethylene takes place at each stage within the coordination sphere of the titanium atom, so monomers can add only at the end of the growing chain. The result is linear polyethylene, also called **high-density polyethylene** (HDPE) because of its density (0.96 g cm^{-3}). Because its linear chains are regular, HDPE contains large crystalline regions, which make it much harder than LDPE and thus suitable for molding into plastic bowls, lids, and toys.

A third kind of polyethylene introduced in the late 1970s is called **linear low-density polyethylene** (LLDPE). It is made by the same metal-catalyzed reactions as HDPE, but it is a deliberate copolymer with other 1-alkenes such as 1-butene. It has some side groups (which reduce the crystallinity and density), but they have a controlled short length instead of the irregular, long side branches in LDPE. LLDPE is stronger and more rigid than LDPE; it is also less expensive because lower pressures and temperatures are used in its manufacture.

If one of the hydrogen atoms of the ethylene monomer unit is replaced with a different type of atom or functional group, the plastics that form upon polymerization have different properties. Substitution of a methyl group (that is, the use of propylene as monomer) leads to polypropylene:



$$\left[CH_2-\underset{CH_3}{\underset{\mid}{CH}}\right]_n$$

This reaction cannot be carried out successfully by free-radical polymerization. It was first achieved in 1953–1954 by Ziegler and the Italian chemist Giulio Natta, who used the Ziegler catalyst later employed in making HDPE. In polypropylene, the methyl groups attached to the carbon backbone can be arranged in different conformations (Fig. 23.6). In the **isotactic form,** all the methyl groups are arranged on the same side, whereas in the **syndiotactic form** they alternate in a regular fashion. The **atactic form** shows a random positioning of methyl groups. Natta showed that the Ziegler catalyst led to isotactic polypropylene, and he developed another catalyst, using VCl_4, that gave the syndiotactic form. Polypropylene plastic is

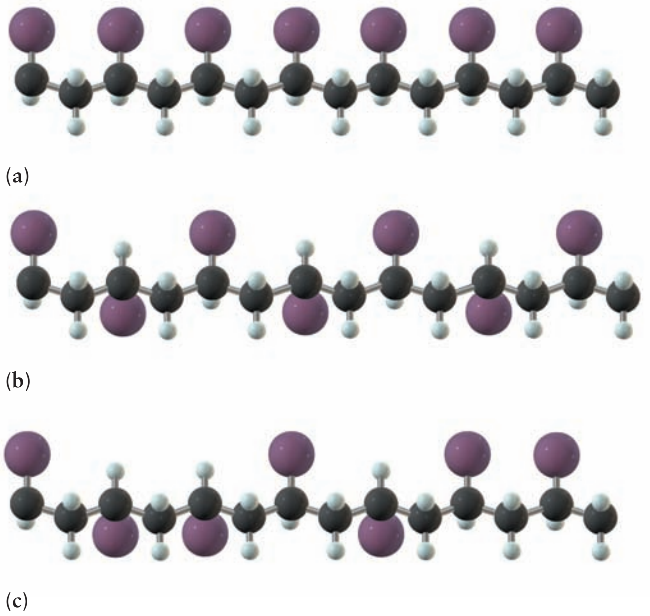


FIGURE 23.6 The structures of (a) isotactic, (b) syndiotactic, and (c) atactic polypropylene. In these structures the purplish-pink spheres represent $-\mathrm{CH}_3$ (methyl) side groups on the long chain.

stiffer and harder than HDPE and has a higher melting point, so it is particularly useful in applications requiring high temperatures (such as the sterilization of medical instruments).

In polystyrene, a benzene ring replaces one hydrogen atom of each ethylene monomer unit. Because such a ring is bulky, atactic polystyrene does not crystallize to any significant extent. The most familiar application of this polymer is in the polystyrene foam used in disposable containers for food and drinks and as insulation. A volatile liquid or a compound that dissociates to gaseous products on heating is added to the molten polystyrene. It forms bubbles that remain as the polymer is cooled and molded. The gas-filled pockets in the final product make it a good thermal insulator.

Synthetic polymers with other elements beyond carbon and hydrogen offer many additional possibilities for making plastics. Polyvinylchloride was already discussed in Section 23.1. Another well-known plastic is the solid perfluorocarbon called polytetrafluoroethylene (Teflon), formulated as $(-\mathrm{CF}_2-\mathrm{CF}_{2-})_n$, where n is a large number. Chemically, this compound is nearly completely inert, resisting attack from boiling sulfuric acid, molten potassium hydroxide, gaseous fluorine, and other aggressive chemicals. Physically, it has excellent heat stability (a working temperature up to 260°C), is a very good electrical insulator, and has a low coefficient of friction that makes it useful for bearing surfaces in machines as well as coating frying pans (“non-stick” Teflon). In Teflon the carbon atoms lie in a long chain that is encased by tightly bound fluorine atoms (Fig. 23.7). Even reactants with a strong innate ability to disrupt C—C bonds (such as fluorine itself) fail to attack Teflon at observable rates because there is no way to get past the surrounding fluorine atoms and their tightly held electrons.

FIGURE 23.7 A model of the molecular structure of Teflon shows that the fluorine atoms shield the carbon chain very effectively. Note that the chain must twist to accommodate the bulk of the fluorine atoms, completing a full spiral every 26 C atoms along the chain.

Rubber

An **elastomer** is a polymer that can be deformed to a great extent and still recover its original form when the deforming stress is removed. The term *rubber* was introduced by Joseph Priestley, who observed that such materials can be used to rub out pencil marks. Natural rubber is a polymer of isoprene (2-methylbutadiene). The isoprene molecule contains two double bonds of which polymerization removes only one; natural rubber is therefore unsaturated, containing one double bond per isoprene unit. In polymeric isoprene, the geometry at each double bond

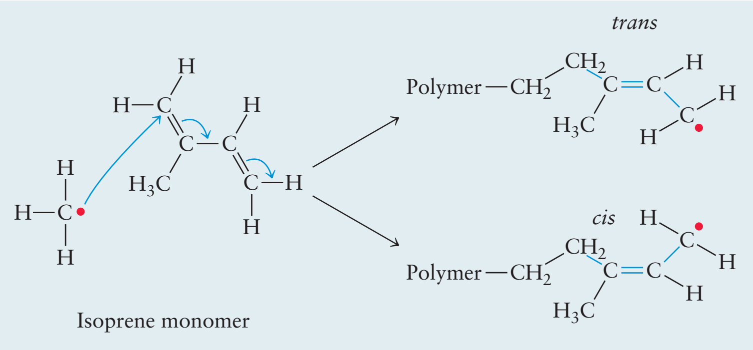


FIGURE 23.8 In the polymerization of isoprene, a *cis* or *trans* configuration can form at each double bond in the polymer. The blue arrows show the redistribution of the electrons upon bond formation.

can be either *cis* or *trans* (Fig. 23.8). Natural rubber is all-*cis* polyisoprene. The all-*trans* form also occurs in nature in the sap of certain trees and is called gutta-percha. This material is used to cover golf balls because it is particularly tough. Isoprene can be polymerized by free-radical addition polymerization, but the resulting polymer contains a mixture of *cis* and *trans* double bonds and is useless as an elastomer.

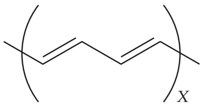
Even pure natural rubber has limited utility because it melts, is soft, and does not fully spring back to its original form after being stretched. In 1839 the American inventor Charles Goodyear discovered that if sulfur is added to rubber and the mixture is heated, the rubber hardens, becomes more resilient, and does not melt. This process is referred to as **vulcanization** and involves the formation of sulfur bridges between the methyl side groups on different chains. Small amounts of sulfur ($<5\%$) yield an elastic material in which sulfur links between chains remain after stretching and enable the rubber to regain its original form when the external force is removed. Large amounts of sulfur give the very hard, nonelastic material ebonite.

Research on synthetic substitutes for natural rubber began in the United States and Europe before World War II. Attention focused on copolymers of butadiene with styrene (now called SBR rubber) and with acrylonitrile (NBR rubber). The Japanese occupation of the rubber-producing countries of Southeast Asia sharply curtailed the supply of natural rubber to the Allied nations, and rapid steps were taken to increase production of synthetic rubber. The initial production goal was 40,000 tons per year of SBR. By 1945, U.S. production had reached an incredible total of more than 600,000 tons per year. During those few years, many advances were made in production techniques, quantitative analysis, and basic understanding of rubber elasticity. Styrene–butadiene rubber production continued after the war, and in 1950 SBR exceeded natural rubber in overall production volume for the first time. More recently, several factors have favored natural rubber: the increasing cost of the hydrocarbon feed stock for synthetic rubber, gains in productivity of natural rubber, and the growing preference for belted radial tires, which use more natural rubber.

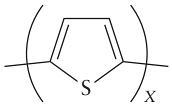
The development of the Ziegler–Natta catalysts has affected rubber production as well. First, it facilitated the synthesis of all-*cis* polyisoprene and the demonstration that its properties were nearly identical to those of natural rubber. (A small amount of "synthetic natural rubber" is produced today.) Second, a new kind of synthetic rubber was developed: all-*cis* polybutadiene. It now ranks second in production after styrene–butadiene rubber.

Electrically Conducting Polymers

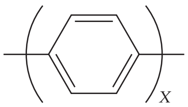
Electrically conducting polymers, sometimes called *synthetic metals,* have a backbone that is a π-conjugated system, with alternating double and single bonds. This system is formed by overlap of carbon $2p_z$-orbitals, as in Figure 7.17. The polymers are named after the monomer units on which their structures are based. The simplest conducting polymer is polyacetylene, which is a continuation of the 1,3-butadiene structure in Figure 7.17 to much longer chain lengths. Other conducting polymers include ring structures in the conjugated backbone. The monomeric units are shown below for *trans*-polyacetylene, polythiophene, poly(*para*-phenylene), and poly(*para*-pyridine).



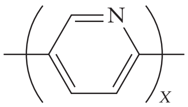
trans-Polyacetylene



Polythiophene



Poly(*para*-phenylene)



Poly(*para*-pyridine)

As the chain length increases, the energy levels shown in Figure 7.17 for 1,3-butadiene increase in number and coalesce into bands. Thus, the conjugated electronic structure for the individual linear polymer molecule is described by bands, which previously we have seen only for extended three-dimensional solids (see Figs. 21.20 and 22.21). The ground state for the polymer chain is that of an insulator, with an energy gap between occupied and empty levels.

The pure polymers are made conductive by doping; the conductivity increases as the doping level increases. Room temperature conductivity for polyacetylene doped with iodine has reached values of 5×10^4 S cm^{-1}, which is about one-tenth the value for copper. (See Section 23.1 for the definition and dimensions of conductivity.) Doping of conductive polymers does not involve substitutional replacement of lattice atoms as in the inorganic semiconductors (see Section 22.7). Rather, doping proceeds by partial oxidation or reduction of the polymer. Electron-donating dopants like Na, K, and Li produce *n*-type material (partly reduced), whereas electron acceptors like I_2, PF_6, and BF_4 produce *p*-type material (partly oxidized). The dopant ions appear interstitially between the polymer chains and promote conductivity by exchanging charges with the conjugated polymer backbones. A wide variety of interesting structural arrangements of polymer chains and dopants can be produced. The details of the conduction process depend strongly on structure and on the degree of ordering of the polymer chains. Research in this area is a fascinating interplay between concepts of solid state physics and synthetic organic chemistry.

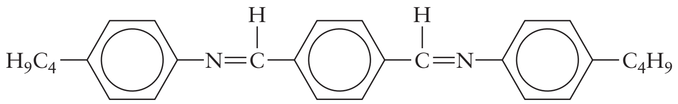
Applications of conductive polymers rely on their combination of electrical and optical properties (comparable to metallic conductors and inorganic semiconductors) with the mechanical flexibility and the chemical processibility of organic polymers. Applications have already appeared in packaging materials for items that are sensitive to electrostatic discharges, in flexible materials for shielding against electromagnetic interference (previously achieved only with rigid metal enclosures), and in rechargeable batteries. Applications are envisioned for electrochemical drug delivery in medicine. Very recent applications include light-emitting diodes, transistors, and memory cells. This field holds rich opportunity for cross-disciplinary developments in chemistry, physics, materials science and engineering, and electrical engineering.

23.3 Liquid Crystals

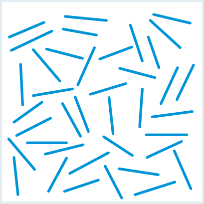
Liquid crystals constitute an interesting state of matter with properties intermediate between those of true liquids and those of crystals. Unlike glasses, liquid-crystal states are thermodynamically stable. Many organic materials do not show a single solid-to-liquid transition but rather a cascade of transitions involving new intermediate phases. In recent years, liquid crystals have been used in a variety of practical applications, ranging from temperature sensors to displays on calculators and other electronic devices.

The Structure of Liquid Crystals

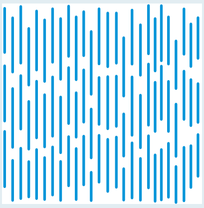
Substances that form liquid crystals are usually characterized by molecules with elongated, rod-like shapes. An example is terephthal-bis-(4-*n*-butylaniline), called TBBA, whose molecular structure can be represented as



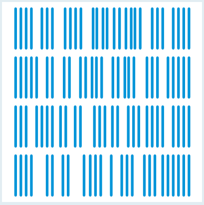
with hydrocarbon groups at the ends separated by a relatively rigid backbone of benzene rings and N=C bonds. Such rod-like molecules tend to line up even in the liquid phase, as Figure 23.9a shows. Ordering in this phase persists only over small distances, however, and on average a given molecule is equally likely to take any orientation.



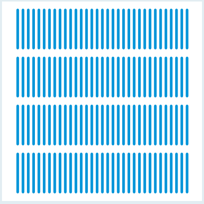
(**a**) Liquid



(**b**) Nematic phase



(**c**) Smectic A phase



(**d**) Molecular crystal

FIGURE 23.9 Different states of structural order for rod-shaped molecules. The figure is only schematic; in a real sample, the lining up of the molecules would not be so nearly perfect.

The simplest type of liquid-crystal phase is the **nematic phase** (see Fig. 23.9b); TBBA undergoes a transition from liquid to nematic at 237°C. In a nematic liquid crystal, the molecules display a preferred orientation in a particular direction, but their centers are distributed at random, as they would be in an ordinary liquid. Although liquid-crystal phases are characterized by a net orientation of molecules over large distances, not all the molecules point in exactly the same direction. There are fluctuations in the orientation of each molecule, and only *on average* do the molecules have a greater probability of pointing in a particular direction.

Some liquid crystals form one or more **smectic phases.** These display a variety of microscopic structures that are indicated by the letters A, B, C, and so forth. Figure 23.9c shows one of them, the smectic A structure; the molecules continue to display net orientational ordering, but now, unlike in the nematic phase, the centers of the molecules also tend to lie in layers. Within each layer, however, these centers are distributed at random as in an ordinary liquid. TBBA enters the smectic A phase at 200°C, before undergoing transitions to two other more ordered smectic phases at lower temperatures.

At low enough temperatures (below 113°C for TBBA), a liquid crystal freezes into a crystalline solid (see Fig. 23.9d) in which the molecules' orientations are ordered and their centers lie on a regular three-dimensional lattice. The progression of structures in Figure 23.9 illustrates the meaning of the term *liquid crystal*. Liquid crystals are solid-like in showing orientational ordering but liquid-like in the random distribution of the centers of their molecules.

A third type of liquid crystal is called **cholesteric.** The name stems from the fact that many of these liquid crystals involve derivatives of the cholesterol molecule. The structure of a cholesteric liquid crystal is shown schematically in Figure 23.10. In each plane the molecules show a nematic type of ordering, but the orientation of the molecules changes by a regular amount from plane to plane, leading to a helical structure. The distance between planes with the same orientations is referred to as the **pitch** *P*, which can be quite large (on the order of hundreds of nanometers or longer). A cholesteric liquid crystal will strongly diffract light with wavelengths λ comparable to the pitch. As the temperature changes, the pitch changes as well; the color of the diffracted light can therefore be used as a simple temperature sensor.

The particular orientation taken by a liquid crystal is very sensitive to both the nature of the surfaces with which it is in contact and small electric or magnetic fields. This sensitivity is the basis for the use of nematic liquid crystals in electronic display devices such as digital watches and calculators (Fig. 23.11), as well as in large-screen liquid-crystal displays.

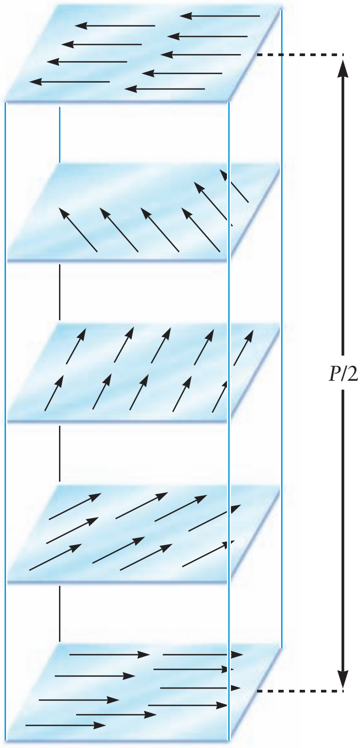


FIGURE 23.10 Several cuts through a cholesteric liquid crystal, showing how the molecular orientation changes with position. The pitch *P* is the distance over which the orientation repeats itself; here, one half of this distance is shown.

Micelles and Membranes

The liquid crystals we have discussed so far have all been single-component systems, but an interesting second type can be formed from two-component mixtures. One component of the mixture is frequently water, and a typical second component is sodium stearate, which has the chemical formula $CH_3(CH_2)_{16}COO^-Na^+$. Preparation of this soap from animal fat was described in Section 7.6. It is a salt analogous to sodium acetate, and its special properties arise from the different natures of the two ends of the molecules. The long hydrocarbon tail is **hydrophobic** ("water fearing") because hydrocarbons do not dissolve in water and avoid contact with it. The ionic carboxylate group ($-COO^-$), on the other hand, is **hydrophilic** and dissolves readily in water both because of its ionic nature and because it can participate in hydrogen bonds. Such molecules are called **amphiphiles.**

If a very small amount of an amphiphile is dissolved in water, it will separate into solvated individual molecules; as soon as a critical concentration is exceeded, however, the molecules organize into **micelles** containing 40 to 100 molecules (Fig. 23.12a). These are small, nearly spherical clusters of molecules whose hydrocarbon tails are in the nonpolar interior and whose ionic groups are exposed to the water. This organization requires a decrease in entropy but leads to a significant lowering of the energy because the hydrophobic chains are removed from direct contact with water. If, on the other hand, a hydrocarbon solvent is used, **reverse micelles** can form, in which the hydrocarbon tails of the long-chain ions make contact with the solvent and small amounts of water are collected in the polar interior of the micelle (see Fig. 23.12b).

Micelle formation is critical to the action of soaps and detergents. Grease and fat are oily substances that are more soluble in hydrocarbons than in pure water. The function of a soap such as sodium stearate in the cleaning of fabrics is to detach the grease and associated materials (dirt) from the surfaces to which it has adhered and to form a suspension of oil drops surrounded by amphiphile molecules, which can then be rinsed off. The main disadvantage of natural soaps is that their salts with ions such as Ca^{2+} and Mg^{2+} (present in dirt or hard water) are not soluble and precipitate, leaving a scum or residue in the objects being washed. To prevent this, a number of analogs to natural soaps have been developed whose calcium and magnesium salts are more soluble in water. Such amphiphilic synthetic agents are called **detergents.**

FIGURE 23.11 The mode of operation of a liquid-crystal display device. (a) The light has a polarization that permits it to pass through the second polarizing filter and strike the mirror, giving a bright display. (b) Imposition of a potential difference across some portion of the display causes the liquid-crystal molecules to rotate, creating a different polarization of light. Because the "rotated" light is blocked by the second filter, it does not reach the mirror, and that part of the display appears black.

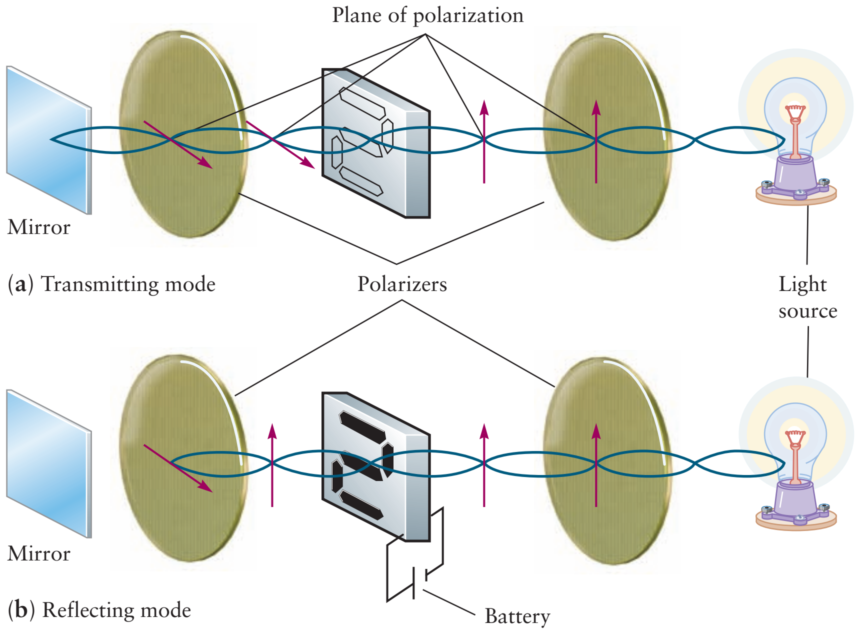
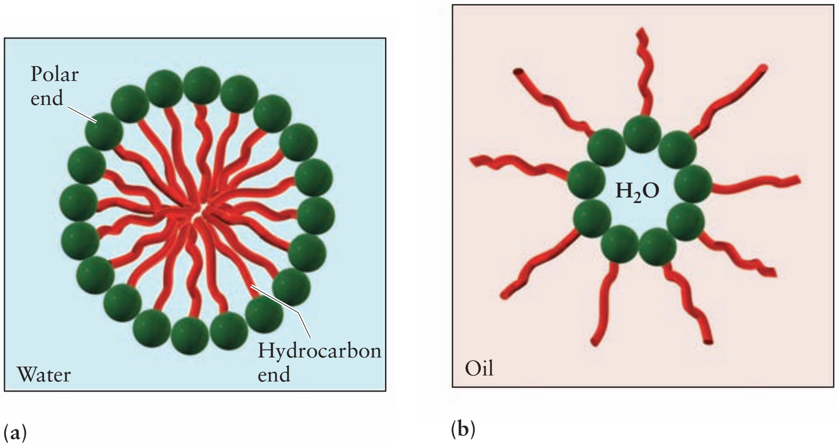


FIGURE 23.12 The structure of a micelle (a) and a reverse micelle (b).



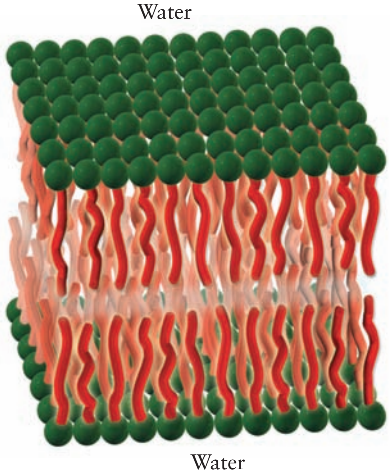


FIGURE 23.13 A bilayer membrane.

Micelles are not the only structures that can form when molecules with hydrophilic and hydrophobic sections are dissolved in water. At higher concentrations, flat **bilayer membranes** form (Fig. 23.13) and can stack into layered, or **lamellar,** phases that resemble smectic liquid crystals in their macroscopic properties. A bilayer membrane consists of two planar layers of molecules, with the hydrophilic portions in contact with water and with the hydrophobic portions of one layer in contact with the corresponding hydrophobic portions of a second layer. Such membranes can be made artificially with detergent solutions and serve as models for biological membranes that enclose living cells. Biological membranes contain embedded proteins that control the passage of ions and molecules through the cell wall. In this way they affect the response of the cell to nerve signals and hormones.

23.4 Natural Polymers

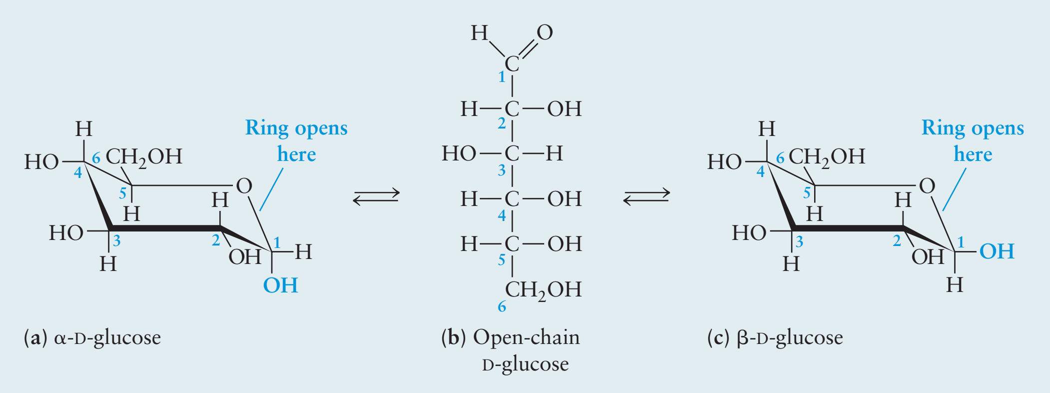
All the products of human ingenuity in the design of polymers pale beside the products of nature. Plants and animals employ a tremendous variety of long-chain molecules with different functions: some for structural strength, others to act as catalysts, and still others to provide instructions for the synthesis of vital components of the cell. In this section we discuss these three important classes of natural polymers: polysaccharides, proteins, and nucleic acids.

Carbohydrates and Polysaccharides

Carbohydrates form a class of compounds of carbon with hydrogen and oxygen. The name comes from the chemical formulas of these compounds, which can be written $C_n(H_2O)_m$, suggesting a “hydrate” of carbon. Simple **sugars,** or **monosaccharides,** are carbohydrates with the chemical formula $C_nH_{2n}O_n$. Sugars with three, four, five, and six carbon atoms are called trioses, tetroses, pentoses, and hexoses, respectively.

Glucose is a hexose sugar that exists in several forms in solution (Fig. 23.14). There is a rapid equilibrium between a straight-chain form (a six-carbon molecule with five —OH groups and one aldehyde —CHO group) and a cyclic form, in which the ring is composed of five carbon atoms and one oxygen, with four —OH side groups and one —CH_2OH side group. In the straight-chain form, four of the carbon atoms (those numbered 2 through 5) are chiral centers, with four different groups bonded to them. As discussed in Section 7.2 (see Fig. 7.9), each such carbon atom can exist in two configurations, each labeled L- for *levo* or D- for *dextro* (Latin for *left* and *right,* respectively). These configurations give rise to $2^4 = 16$

FIGURE 23.14 D-Glucose exists in two ring forms in solution (a and c), which interconvert via an open-chain form (b). The two rings differ in the placement of the —OH and —H groups on carbon atom 1.

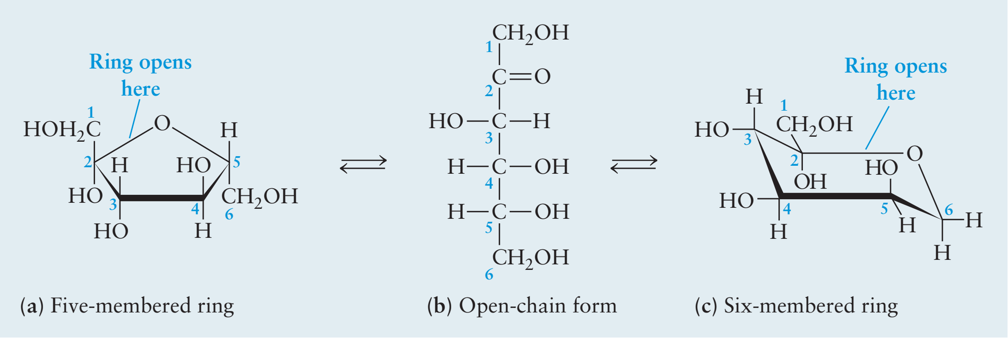


distinct hexose sugars. The glucose formed in plant photosynthesis always has the chirality shown in Figure 23.14b. Of the 15 other straight-chain hexose sugars, the only ones found in nature are D-galactose (in the milk sugar lactose) and D-mannose (a plant sugar).

Figure 23.14 shows that glucose actually has two different ring forms, depending on whether the —OH group created from the aldehyde by the closing of the ring lies above or below the plane of the ring. Another way to see this is to note that closing the ring creates a fifth chiral carbon atom. The two ring forms of D-glucose are called *α*-D-glucose (Fig. 23.14a) and *β*-D-glucose (see Fig. 23.14c). In aqueous solution, these two forms interconvert rapidly via the open-chain glucose form and cannot be separated. They can be isolated separately in crystalline form, however. D-fructose, a common sugar found in fruit and honey, has the same molecular formula as D-glucose but is a member of a class of hexose sugars that are ketones rather than aldehydes. In their straight-chain forms, these sugars have the C=O bond at carbon atom 2 rather than carbon atom 1 (Fig. 23.15).

Many plant cells do not stop the synthesis process with simple sugars such as glucose, but rather continue by linking sugars together to form more complex carbohydrates. **Disaccharides** are composed of two simple sugars linked together by a condensation reaction with the elimination of water. Examples shown in Figure 23.16 are the milk sugar lactose and the plant sugar sucrose (ordinary table sugar, extracted from sugarcane and sugar beets). Further linkages of sugar units lead to polymers called **polysaccharides.** The position of the oxygen atom linking the monomer units has a fundamental effect on the properties and functions of the polymers that result. Starch (Fig. 23.17a) is a polymer of *α*-D-glucose and is metabolized by humans and animals. Cellulose (see Fig. 23.17b), a polymer of *β*-D-glucose, cannot be digested except by certain bacteria that live in the digestive tracts of goats, cows, and other ruminants and in some insects, such as termites. It forms the structural fiber of trees and plants and is present in linen, cotton, and paper. It is the most abundant organic compound on earth.

FIGURE 23.15 In aqueous solutions of the sugar D-fructose, an equilibrium exists among a five-atom ring, an open chain, and a six-atom ring. In addition to the *β* isomers shown here, both ring forms have *α* isomers, in which the —CH_2OH and —OH on carbon 2 are exchanged.



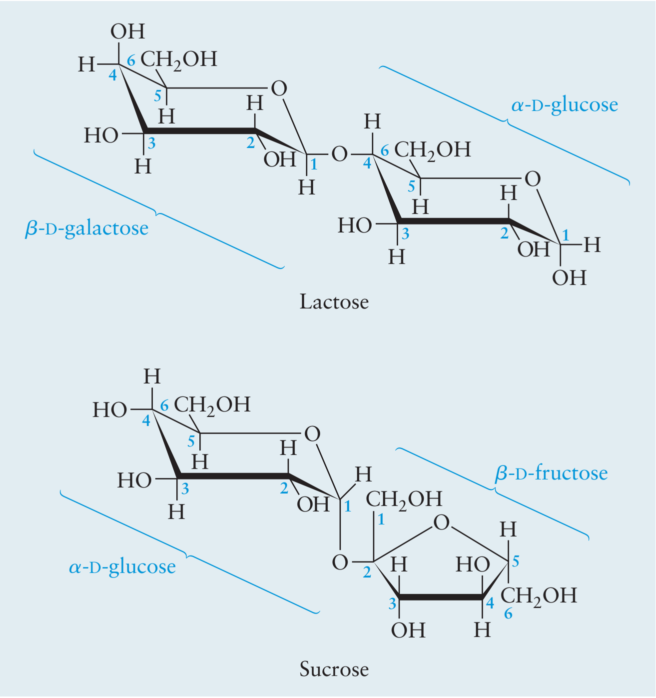


FIGURE 23.16 Two disaccharides. Their derivations from monosaccharide building blocks are shown.

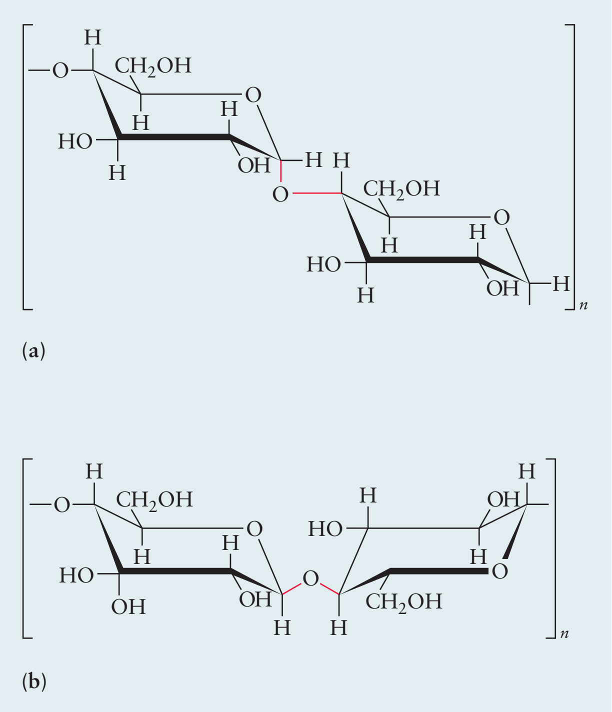


FIGURE 23.17 Both starch (a) and cellulose (b) are polymers of glucose. In starch, all the cyclic glucose units are α-D-glucose. In cellulose, all the monomer units are β-D-glucose.

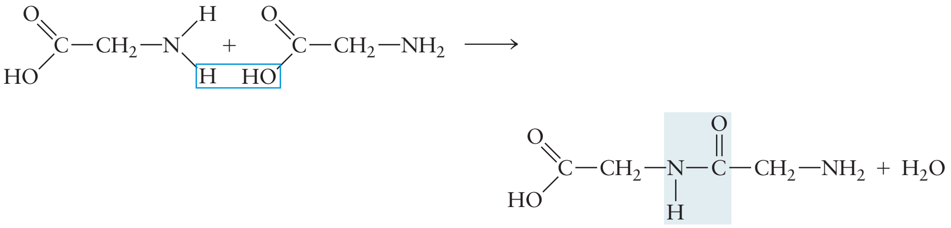
Amino Acids and Proteins

The monomeric building blocks of the biopolymers, called proteins, are the α-amino acids. The simplest amino acid is glycine, which has the molecular structure shown in Figure 23.18. An amino acid, as indicated by the name, must contain an amine group ($-NH_2$) and a carboxylic acid group ($-COOH$). In α-amino acids, the two groups are bonded to the same carbon atom. In acidic aqueous solution, the amine group is protonated to form $-NH_3^+$; in basic solution, the

FIGURE 23.18 The structure of glycine. On the left side is the carboxylic acid group (—COOH), and on the right is the amine group (—NH_2).

carboxylic acid group loses a proton to form $-COO^-$. At intermediate pH, both reactions occur. The net result is that the simple amino acid form shown in Figure 23.18 is almost never present in aqueous solution (see Problem 27).

Two glycine molecules can condense with loss of water to form an amide:



The amide functional group connecting two amino acids is referred to as a **peptide linkage,** and the resulting molecule is a *dipeptide*—in this case, diglycine. Because the two ends of the molecule still have carboxylic acid and amine groups, further condensation reactions to form a **polypeptide,** a polymer comprised of many amino acid groups, are possible. If glycine were the only amino acid available, the result would be polyglycine, a rather uninteresting protein. There is a close similarity between this naturally occurring condensation polymer and the synthetic polyamide nylon. Polyglycine could be called "nylon 2," a simple polyamide in which each repeating unit contains two carbon atoms.

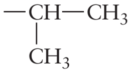
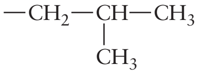
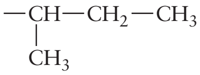
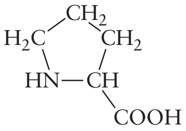
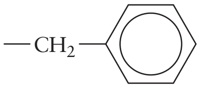
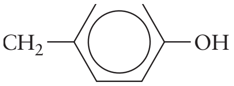
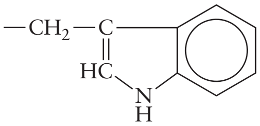
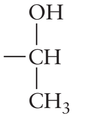
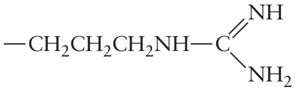
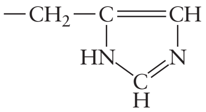
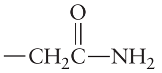
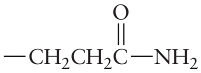
Nature does not stop with glycine as a monomer unit. Instead, any of 20 different α-amino acids are found in most natural polypeptides. In each of these, one of the hydrogen atoms on the central carbon atom of glycine is replaced by another side group. Alanine is the next simplest α-amino acid after glycine; it has a $-CH_3$ group in place of an $-H$ atom. This substitution has a profound consequence. In alanine, four different groups are attached to a central carbon: $-COOH$, $-NH_2$, $-CH_3$, and $-H$. There are two ways in which four different groups can be arranged in a tetrahedral structure about a central atom (see Fig. 7.9). The two optical isomers of alanine are designated by the prefixes L- and D- for *levo* and *dextro* (Latin for "left" and "right," respectively).

If a mixture of L- and D-alanine were caused to polymerize, nearly all the polymer molecules would have different structures because their sequences of D-alanine and L-alanine monomer units would differ. To create polymers with definite structures for particular roles, there is only one recourse: to build all polypeptides from one of the optical isomers so that the properties will be reproducible from molecule to molecule. Nearly all naturally occurring α-amino acids are of the L form, and most earthly organisms have no use for D-α-amino acids in making polypeptides. Terrestrial life could presumably have begun equally well using mainly D-amino acids (all biomolecules would be mirror images of their present forms). The mechanism by which the established preference was initially selected is not known.

The $-H$ group of glycine and $-CH_3$ group of alanine give just the first two amino acid building blocks. Table 23.3 shows all 20 important α-amino acids, arranged by side group. Note the variety in their chemical and physical properties. Some side groups contain basic groups; others are acidic. Some are compact; others are bulky. Some can take part in hydrogen bonds; others can complex readily with metal ions to form coordination complexes.

This variety in properties of the α-amino acids leads to even more variety in the polymers derived from them, called **proteins.** The term *protein* is usually applied to polymers with more than about 50 amino acid groups; large proteins may contain many thousand such groups. Given the fact that any one of 20 α-amino acids may appear at each point in the chain, the number of possible sequences of amino acids in even small proteins is staggering. Moreover, the amino acid sequence describes only one aspect of the molecular structure of a protein. It contains no information about the three-dimensional conformation adopted by the protein. The carbonyl group and the amine group in each amino acid along the

TABLE 23.3 *α*-Amino Acid Side Groups

	Symbol	Structure of Side Group
Hydrogen "Side Group"		
Glycine	Gly	$-\mathrm{H}$
Alkyl Side Groups		
Alanine	Ala	$-\mathrm{CH_3}$
Valine	Val	 $-\underset{\substack{\vert\\ \mathrm{CH_3}}}{\mathrm{CH}}-\mathrm{CH_3}$
Leucine	Leu	 $-\mathrm{CH_2}-\underset{\substack{\vert\\ \mathrm{CH_3}}}{\mathrm{CH}}-\mathrm{CH_3}$
Isoleucine	Ile	 $-\underset{\substack{\vert\\ \mathrm{CH_3}}}{\mathrm{CH}}-\mathrm{CH_2}-\mathrm{CH_3}$
Proline	Pro (structure of entire amino acid)	
Aromatic Side Groups		
Phenylalanine	Phe	
Tyrosine	Tyr	
Tryptophan	Trp	
Alcohol-Containing Side Groups		
Serine	Ser	$-\mathrm{CH_2OH}$
Threonine	Thr	 $-\overset{\substack{\mathrm{OH}\\ \vert}}{\underset{\substack{\vert\\ \mathrm{CH_3}}}{\mathrm{CH}}}$
Basic Side Groups		
Lysine	Lys	$-\mathrm{CH_2CH_2CH_2CH_2NH_2}$
Arginine	Arg	
Histidine	His	
Acidic Side Groups		
Aspartic acid	Asp	$-\mathrm{CH_2COOH}$
Glutamic acid	Glu	$-\mathrm{CH_2CH_2COOH}$
Amide-Containing Side Groups		
Asparagine	Asn	 $-\mathrm{CH_2}\overset{\substack{\mathrm{O}\\ \Vert}}{\mathrm{C}}-\mathrm{NH_2}$
Glutamine	Gln	 $-\mathrm{CH_2CH_2}\overset{\substack{\mathrm{O}\\ \Vert}}{\mathrm{C}}-\mathrm{NH_2}$
Sulfur-Containing Side Groups		
Cysteine	Cys	$-\mathrm{CH_2}-\mathrm{SH}$
Methionine	Met	$-\mathrm{CH_2CH_2}-\mathrm{S}-\mathrm{CH_3}$

protein chain are potential sites for hydrogen bonds, which may also involve functional groups on the amino acid side chains. Also, the cysteine side groups ($-CH_2-SH$) can react with one another, with loss of hydrogen, to form $-CH_2-S-S-CH_2-$ disulfide bridges between different cysteine groups in a single chain or between neighboring chains (the same kind of cross-linking by sulfur occurs in the vulcanization of rubber). As a result of these strong intrachain interactions, the molecules of a given protein have a rather well-defined conformation even in solution, as compared with the much more varied range of conformations available to a simple alkane chain (see Fig. 7.3). The three-dimensional structures of many proteins have been determined by x-ray diffraction.

There are two primary categories of proteins: fibrous and globular. **Fibrous proteins** are usually structural materials and consist of polymer chains linked in sheets or twisted in long fibers. Silk is a fibrous protein in which the monomer units are primarily glycine and alanine, with smaller amounts of serine and tyrosine. The protein chains are cross-linked by hydrogen bonds to form sheet-like structures (Fig. 23.19) that are arranged so that the nonhydrogen side groups all lie on one side of the sheet; the sheets then stack in layers. The relatively weak forces between sheets give silk its characteristic smooth feel. The amino acids in wool and hair have side chains that are larger, bulkier, and less regularly distributed than those in silk; therefore, sheet structures do not form. Instead, the protein molecules twist into a right-handed coil called an α-**helix** (Fig. 23.20). In this

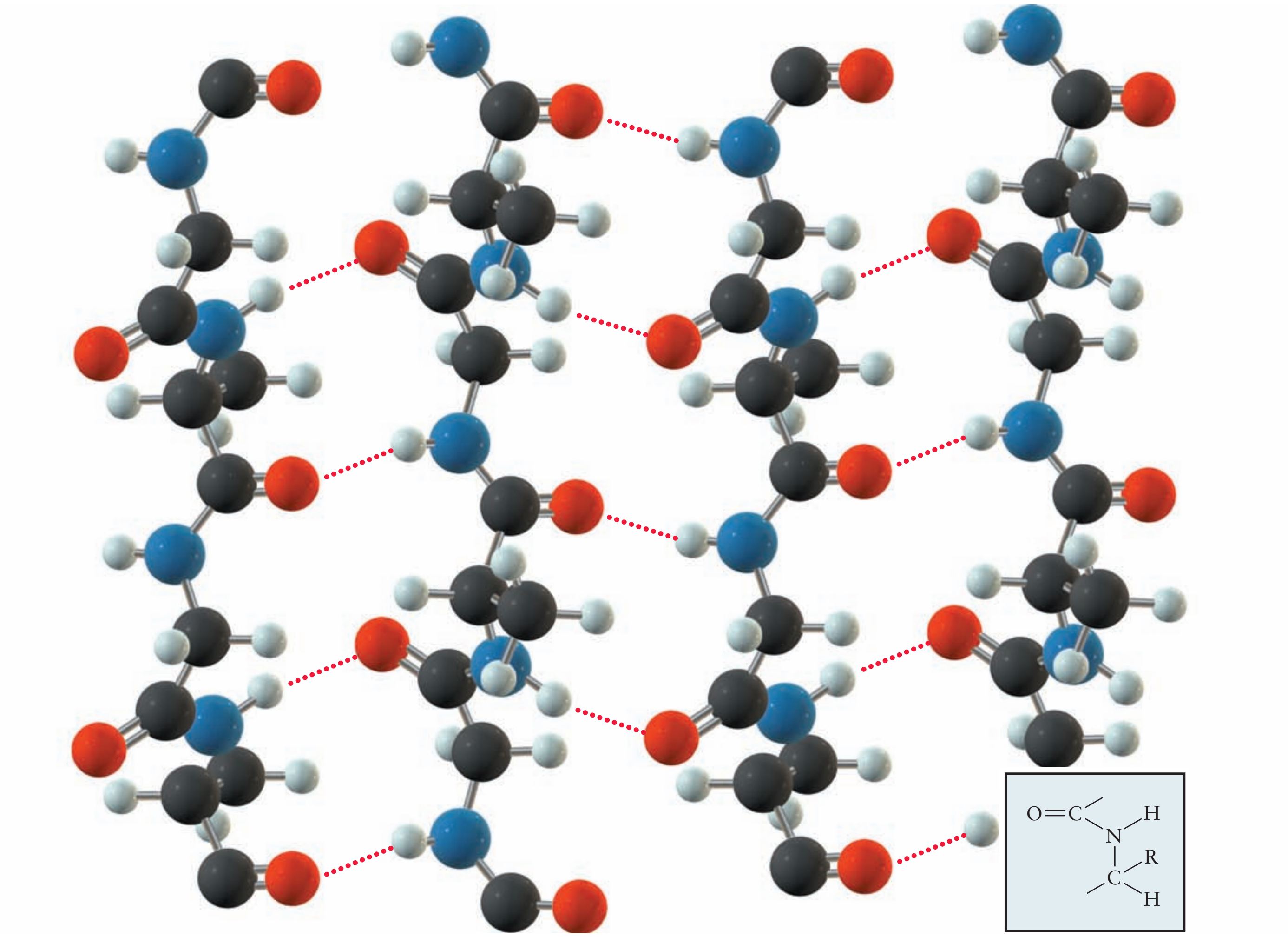


FIGURE 23.19 The structure of silk. The amino acid side groups (shown as R) must be small to fit into a sheet-like structure. Glycine (R=H) and alanine ($R=CH_3$) predominate. The repeating unit is shown as an inset.

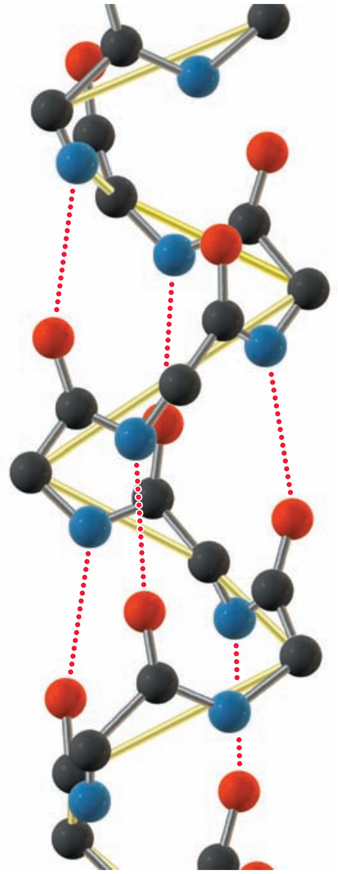


FIGURE 23.20 The structure of an α-helix for a stretch of linked glycine monomer units. The superimposed yellow line highlights the helical structure, which is maintained by hydrogen bonds (red dotted lines). The hydrogen atoms themselves are omitted for clarity.

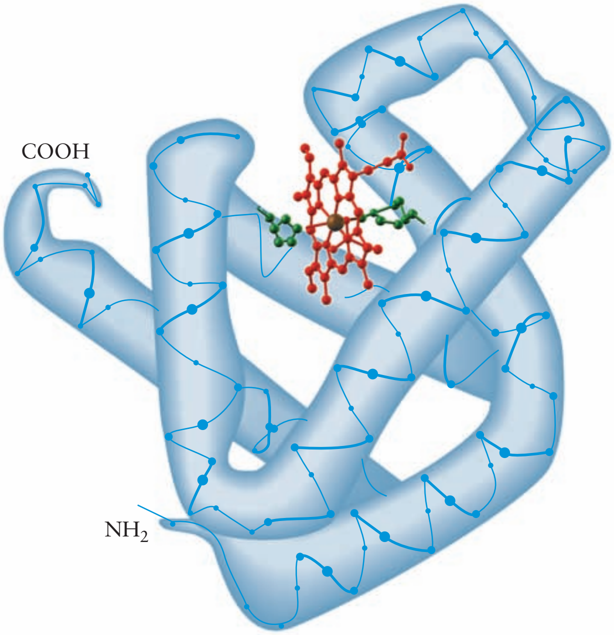
structure, each carbonyl group is hydrogen-bonded to the amine group of the fourth amino acid farther along the chain; the bulky side groups jut out from the helix and do not interfere with one another.

The second type of protein is the **globular protein.** Globular proteins include the carriers of oxygen in the blood (hemoglobin) and in cells (myoglobin). They have irregular folded structures (Fig. 23.21) and typically consist of 100 to 1000 amino acid groups in one or more chains. Globular proteins frequently have parts of their structures in α-helices and sheets, with other portions in more disordered forms. Hydrocarbon side groups tend to cluster in regions that exclude water, whereas charged and polar side groups tend to remain in close contact with water. The sequences of amino acid units for many such proteins have been worked out by cleaving them into smaller pieces and analyzing the structure of the fragments. It took Frederick Sanger 10 years to complete the first such determination of sequence for the 51 amino acids in bovine insulin, an accomplishment that earned him the Nobel Prize in chemistry in 1958. Now, automated procedures enable scientists to rapidly determine amino acid sequences in much longer protein molecules.

Enzymes constitute a very important class of globular proteins. They catalyze particular reactions in the cell, such as the synthesis and breakdown of proteins, the transport of substances across cell walls, and the recognition and resistance of foreign bodies. Enzymes act by lowering the activation barrier for a reaction, and they must be selective so as to act only on a restricted group of substrates.

Let's examine the enzyme carboxypeptidase A, whose structure has been determined by x-ray diffraction. It removes amino acids one at a time from the carboxylic acid end of a polypeptide. Figure 23.22 shows the structure of the active site (with a peptide chain in place, ready to be cleaved). A special feature of this enzyme is the role played by the zinc ion, which is coordinated to two histidine residues in the enzyme and to a carboxylate group on a nearby glutamic acid residue. The zinc ion helps remove electrons from the carbonyl group of the peptide linkage, making it more positive and thereby more susceptible to attack by water or by the carboxylate group of a second glutamic acid residue. The side chain on the outer amino acid of the peptide being cleaved is positioned in a hydrophobic cavity, which favors large aromatic or branched side chains (such as that in tyrosine) over smaller hydrophilic side chains (such as that in aspartic acid). Carboxypeptidase A is thus selective about the sites at which it cleaves peptide chains.

FIGURE 23.21 A computer-generated model of the structure of myoglobin. The central heme group (red) is shown in greater detail in Figure 8.22; two histidine groups (green) extend toward the central iron atom. Much of the protein (blue tube) is coiled in α-helices.



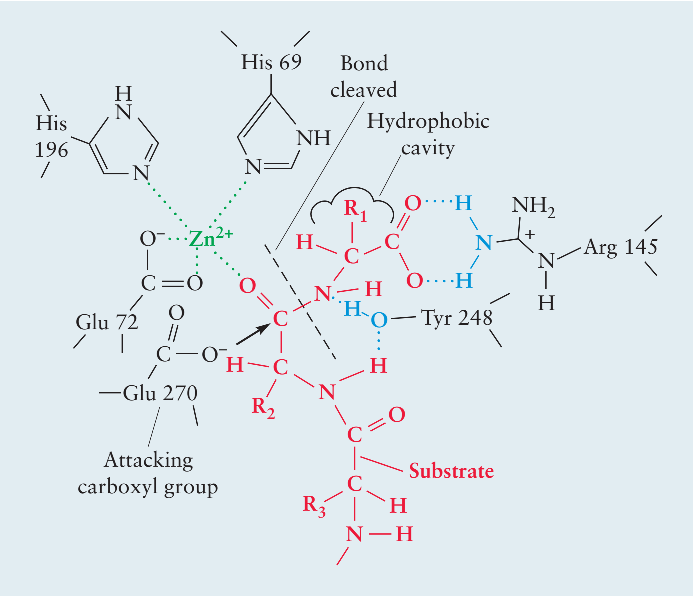


FIGURE 23.22 The active site of carboxypeptidase A. Shown in red is a substrate polypeptide that is being cleaved by the enzyme. Green is used to show the role of Zn^{2+} as a complexing ion, and blue is used to show the hydrogen bonds that maintain the geometry.

The molecular "engineering" that lies behind nature's design of carboxypeptidase A and other enzymes is truly remarkable. The amino acid residues that form the active site and determine its catalytic properties are *not* adjacent to one another in the protein chain. As indicated by the numbers after the residues in Figure 23.22, the two glutamic acid residues are the 72nd and 270th amino acids along the chain. The enzyme adopts a conformation in which the key residues, distant from one another in terms of chain position, are nonetheless quite close in three-dimensional space, allowing the enzyme to carry out its specialized function.

Nucleotides and Nucleic Acids

We have seen that proteins are copolymers made up typically of 20 types of monomer units. Simply mixing the amino acids and letting them dehydrate to form polymer chains at random would never lead to the particular structures needed by living cells. How does the cell preserve information about the amino acid sequences that make up its proteins, and how does it transmit this information to daughter cells through the reproductive process? These questions lie in the field of molecular genetics, an area in which chemistry plays the central role.

The primary genetic material is deoxyribonucleic acid (DNA). This biopolymer is made up of four types of monomer units called **nucleotides.** Each nucleotide is composed of three parts:

1. One molecule of a pyrimidine or purine base. The four bases are thymine, cytosine, adenine, and guanine (Fig. 23.23a).
2. One molecule of the sugar D-deoxyribose ($C_5H_{10}O_4$). D-Ribose is a pentose sugar with a five-membered ring.
3. One molecule of phosphoric acid (H_3PO_4).

The cyclic sugar molecule links the base to the phosphate group, undergoing two condensation reactions, with loss of water, to form the nucleotide (see Fig. 23.23b). The first key to discovering the structure of DNA was the following observation: Although the proportions of the four bases in DNA from different organisms are quite variable, the chemical amount of cytosine (C) is always approximately equal to that of guanine (G) and the chemical amount of adenine (A) is always approximately equal to that of thymine (T). This suggested some type of base pairing in DNA that could lead to association of C with G and of A with T. The second crucial observation was an x-ray diffraction study by Rosalind

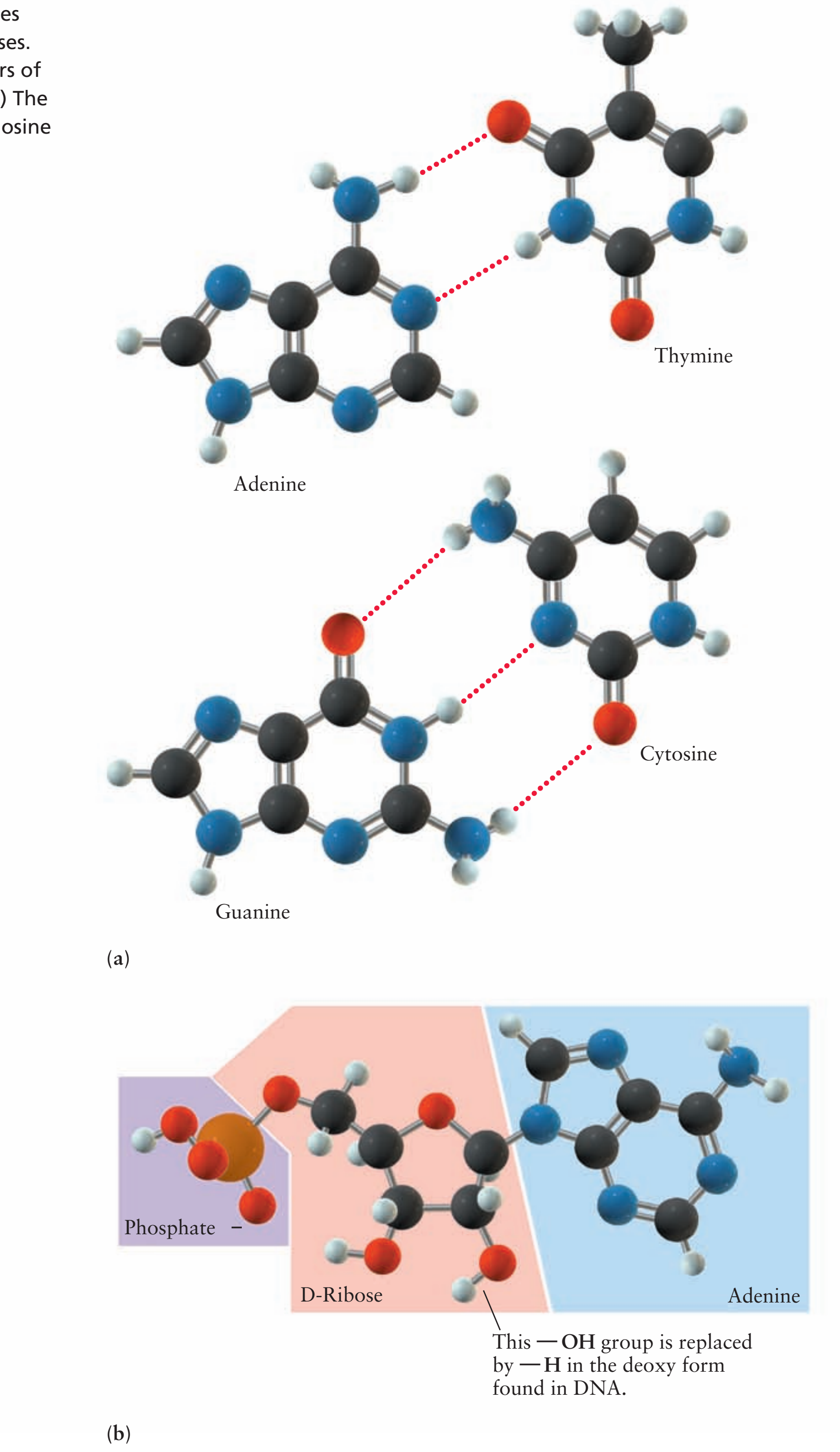
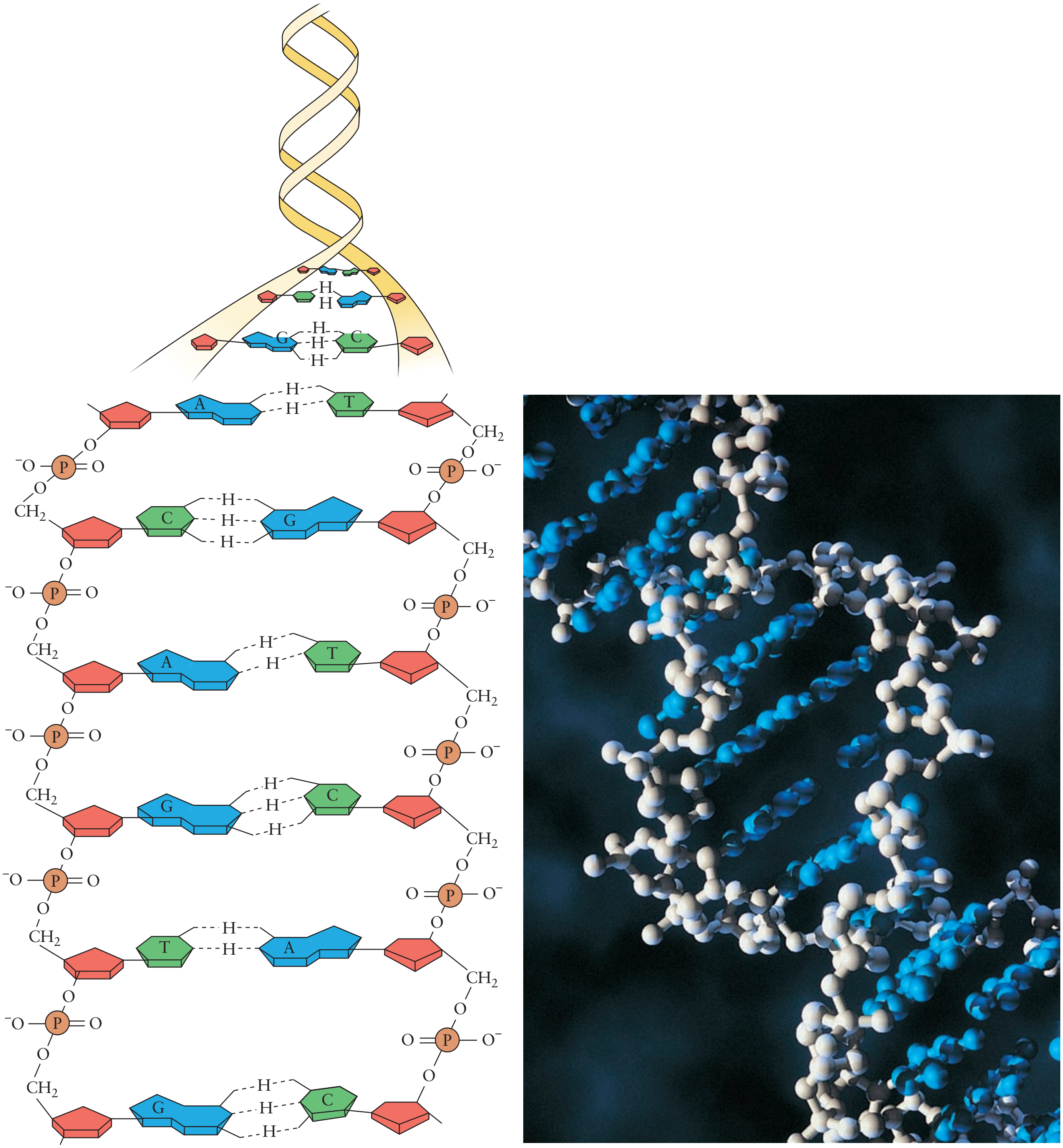


FIGURE 23.23 (a) The structures of the purine and pyrimidine bases. Hydrogen-bonding between pairs of bases is indicated by red dots. (b) The structure of the nucleotide adenosine monophosphate (AMP).

Franklin and Maurice Wilkins that suggested the presence of helical structures of more than one chain in DNA.

James Watson and Francis Crick put together these two pieces of information in their famous 1953 proposal of a double-helix structure for DNA. They concluded that DNA consists of two interacting helical strands of nucleic acid polymer (Fig. 23.24), with each cytosine on one strand linked through hydrogen bonds to a guanine on the other and each adenine to a thymine. This accounted for the observed molar ratios of the bases, and it also provided a model for the replication of the molecule, which is crucial for passing on information during the reproductive process. One DNA strand serves as a template upon which a second DNA strand is synthesized. A DNA molecule reproduces by starting to unwind at one end. As it does so, new nucleotides are guided into position opposite the proper bases on each of the two strands. If the nucleotide does not fit the template, it cannot link to the polymeric strand under construction. The result of the polymer synthesis is two double-helix molecules, each containing one strand from the original and one new strand that is identical to the original in every respect.



Right, © Kenneth Edward/Biografx/Photo Researchers, Inc.

FIGURE 23.24 The double-helix structure of DNA.

Information is encoded in DNA in the sequence of the base pairs. Subsequent research has broken this genetic code and established the connection between the base sequence in a segment of DNA and the amino acid sequence of the protein synthesized according to the directions in that segment. The code in a nucleic acid is read as consecutive, nonoverlapping triplets of bases, with each triplet standing for a particular amino acid. Thus, a nucleic acid strand consisting of pure cytosine gives a polypeptide of pure proline, meaning that the triplet CCC codes for proline. The nucleic acid strand AGAGAGAG . . . is read as the alternating triplets AGA and GAG and gives a polypeptide consisting of alternating arginine (coded by AGA) and glutamic acid (coded by GAG) monomer units. There are 64 (4^3) possible triplets, so typically more than one code exists for a particular amino acid. Some triplets serve as signals to terminate a polypeptide chain. Remarkably, the genetic code appears to be universal, independent of the species of plant or animal, a finding that suggests a common origin for all terrestrial life.

A single change in a base pair in DNA causes a change in one amino acid of the protein that is coded for by that DNA. Such a change may seem small, but it may have dramatic (even fatal) effects for the organism in question. For example, the triplets GAA and GAG both code for glutamic acid (an acidic residue), whereas the triplets GTA and GTG code for valine (a nonpolar residue). A single change in the central A to T in the DNA thus changes an amino acid in a protein produced by the organism. This might seem like a small effect, but it can change the structure and mode of action of the protein. This particular change is responsible for the presence of hemoglobin S (instead of hemoglobin A) in the blood of people who have sickle cell anemia. In two of the four hemoglobin S chains a glutamic acid amino acid is changed to a valine, and the result is a decrease in the solubility of S relative to A by a factor of 25. This leads to polymerization of the hemoglobin to form insoluble structures that bend red blood cells into sickle shapes, a change that can lead to early death. One of the challenges of modern genetic engineering is to use chemistry to modify coding molecules in living species to eliminate fatal or disease-causing mutants.

CHAPTER SUMMARY

Mankind has long used naturally occurring polymers, obtained from plants and animals, as useful materials. These are familiar in cotton, wool, and silk fabrics, and in structural applications of wood and rubber. Inspired by these natural products, chemists have invented synthetic routes to these and similar materials, often with modified or improved properties. Curiosity about life processes in living systems has inspired research on natural polymers, such as polysaccharides, proteins, enzymes, and DNA, to discern the relation between their structure and function. The structures of these solid synthetic and natural polymeric materials range from purely amorphous to highly crystalline. The route to controlling their molecular and crystalline structures lies through understanding their local bonding.

CHAPTER REVIEW

- Polymer formation requires that many monomers must be attached to a growing polymer molecule. This requires that highly reactive functional groups must be available at each growth step. This is achieved by two main mechanisms.
  Addition polymerization requires monomers to join the polymer without net loss of atoms. This usually involves free radical reaction of molecules that have C=C double bonds, and proceeds through three steps: initiation, propagation, and termination.

  Condensation polymerization requires that a small molecule such as water is split off as each monomer is added to the polymer.
  Both addition and condensation polymerization can occur with mixtures of monomers to produce a random copolymer of the two monomers.
  If monomers have three or more reactive sites, cross-linking reactions to form sheets or networks is possible. Cross-linking is often brought about deliberately to obtain stronger materials.

- Synthetic polymers are selected for four major classes of applications based on their physical properties
  Fibers for use in fabrics are spun into threads in which their molecules are aligned. They must resist stretching, and usually break after only 10% elongation. The first purely synthetic fiber was nylon, developed by condensation polymerization.
  Plastics are molded or extruded into desired shapes that harden upon cooling or solvent evaporation. They typically elongate 20% to 100% before breaking. Many of these are formed by addition polymerization of ethylene or its derivatives. Examples include polyethylene, polystyrene, and Teflon. By using proper catalysts and manipulating the size of side group substituents, it is possible to overcome the tendency of addition polymerization to form highly branched chains. These tools make it possible to control the degree of crystallinity in polymer materials.
  Rubbers, or elastomers, stretch readily to elongate by a factor of 10 before breaking. Natural rubber, obtained from the sap of certain trees, can be hardened and toughened by addition of sulfur in the vulcanization process. Synthetic rubber is produced by addition copolymerization of butadiene and styrene.
  Electrically conducting polymers combine the optical and electronic properties of inorganic semiconductors with the processing ease of conventional polymers. Their structures are continuations of the 1,3-butadiene structure to greater lengths, and the electronic structure for the individual molecule is described by bands. These polymers are made electrically conducting by doping.

- Liquid crystals have properties intermediate between those of true liquids and crystals. Unlike glasses, they are thermodynamically stable.
  Based on microscopic structural details liquid crystals form three separate ordered phases: nematic, smectic, and cholesteric.
  Orientation of liquid crystals depends sensitively on small electric and magnetic fields. This is the basis of liquid crystal displays for digital information.

- Naturally occurring polymers are synthesized by plants and animals to support a variety of life processes.
  Polysaccharides are grown by linkage of simple sugar units (carbohydrates). One example is starch, which is readily metabolized by humans and animals. Another is cellulose, which forms the structural fibers of plants and trees and appears in linen and cotton fabrics and in paper.
  The biological polymers called proteins are built up from the amino acid units, ranging in number from 50 to several thousand per polymer. Since 20 amino acids are available, a very large number of sequences can be realized. Fibrous proteins consist of polymers linked in sheets or twisted in long fibers; they are structural materials. Globular proteins include hemoglobin and enzymes; they generally control chemical reactions in living systems.
  The primary genetic material DNA is a biopolymer made up of four types of monomer units called nucleotides. DNA serves as a template during reproduction to enable a cell to preserve information about the amino acid sequences that make up its proteins, and transfer this information to daughter cells through the genetic code.

CONCEPTS & SKILLS

After studying this chapter and working the problems that follow, you should be able to:

1. Contrast the methods of addition and condensation polymerization (Section 23.1, Problems 1–6).
2. Give several examples of fibers, plastics, and rubbers and describe how they are made and used (Section 23.2, Problems 7–10).
3. Explain what a liquid crystal is, and state how nematic and smectic phases differ from ordinary liquids and crystalline solids (Section 23.3, Problems 11-12).
4. Describe the formation of ordered structures such as micelles and membranes in surfactant solutions (Section 23.3 Problems 13-14).
5. Describe the formation of polysaccharides from sugars, proteins from amino acids, and DNA from nucleotides and the roles of these biopolymers in living cells (Section 23.4, Problems 15–22).

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G. Problems that are more challenging are indicated with asterisks.

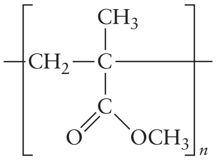
Polymerization Reactions for Synthetic Polymers

1. Write a balanced chemical equation to represent the addition polymerization of 1,1-dichloroethylene. The product of this reaction is Saran, used as a plastic wrap.

2. Write a balanced chemical equation to represent the addition polymerization of tetrafluoroethylene. The product of this reaction is Teflon.

3. A polymer produced by addition polymerization consists of ($-CH_2-O-$) groups joined in a long chain. What was the starting monomer?

4. The polymer polymethyl methacrylate is used to make Plexiglas. It has the formula



Draw the structural formula of the starting monomer.

5. The monomer glycine (NH_2-CH_2-COOH) can undergo condensation polymerization to form polyglycine, in which the structural units are joined by amide linkages.
(a) What molecule is split off in the formation of polyglycine?
(b) Draw the structure of the repeat unit in polyglycine.

6. The polymer forms  $\left(\mathrm{NH-CH(CH_3)-}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\right)_n$ upon condensation polymerization with loss of water. Draw the structure of the starting monomer.

Applications for Synthetic Polymers

7. Determine the mass of adipic acid and the mass of hexamethylenediamine needed to make 1.00×10^3 kg of nylon 66 fiber.

8. Determine the mass of terephthalic acid and the mass of ethylene glycol needed to make 10.0 kg of polyester fiber.

9. In a recent year, 4.37 billion kilograms of low-density polyethylene was produced in the United States. What volume of gaseous ethylene at 0°C and 1.00 atm would give this amount?

10. In a recent year, 2.84 billion kilograms of polystyrene was produced in the United States. Polystyrene is the addition polymer formed from the styrene monomer, $C_6H_5CH{=}CH_2$. How many styrene monomer units were incorporated in that 2.84 billion kilograms of polymer?

Liquid Crystals

11. Compare the natures and extents of order in the smectic liquid-crystal and isotropic liquid phases of a substance. Which has the higher entropy? Which has the higher enthalpy?

12. Nematic liquid crystals form when a liquid of long rod-like molecules is cooled. What *additional* types of intermolecular interactions would you expect to favor the formation of a *smectic* phase?

13. Consider a ternary (three-component) system of amphiphile, hydrocarbon, and water. What structure do you expect to form if small amounts of the first two components are mixed with a large amount of water?

14. In addition to spherical micelles and lamellar phases, a binary amphiphile-water mixture can also form extended cylindrical rolls, with the hydrophilic groups pointing out and the hydrophobic chains on the interior. Over what composition range are such cylinders most likely to be found, relative to spherical micelles and planar layers?

Natural Polymers

15. By referring to Figure 23.16a, draw the structure of the ring form of β-D-galactose. How many asymmetric carbon atoms (chiral centers) are there in the molecule?

16. By referring to Figure 23.23b, draw the structure of the ring form of D-ribose. How many asymmetric carbon atoms (chiral centers) are there in the molecule?

17. How many tripeptides can be synthesized using just three different species of α-amino acids?

18. How many different polypeptides, each containing ten amino acids, can be made from the amino acids listed in Table 23.3? How many different polypeptides, each containing 100 amino acids, can be made?

19. Draw the structure of the pentapeptide alanine—leucine—phenylalanine—glycine—isoleucine. Assume that the free $-NH_2$ group is at the alanine end of the peptide chain. Would this compound be more likely to dissolve in water or in octane? Explain.

20. Draw the structure of the pentapeptide aspartic acid—serine—lysine—glutamic acid—tyrosine. Assume that the free $-NH_2$ group is at the aspartic acid end of the peptide chain. Would this compound be more likely to dissolve in water or in octane? Explain.

21. Suppose a long-chain polypeptide is constructed entirely from phenylalanine monomer units. What is its empirical formula? How many amino acids does it contain if its molar mass is 17,500 g mol^{-1}?

22. A typical bacterial DNA has a molar mass of 4×10^9 g mol^{-1}. Approximately how many nucleotides does it contain?

ADDITIONAL PROBLEMS

23. In the addition polymerization of acrylonitrile, a very small amount of butyl lithium causes a reaction that can consume hundreds of pounds of the monomer; however, the butyl lithium is called an initiator, not a catalyst. Explain why.

24. Based on the facts that the free-radical polymerization of ethylene is spontaneous and that polymer molecules are less disorganized than the starting monomers, decide whether the polymerization reaction is exothermic or endothermic. Explain.

25. According to a trade journal, approximately 950 million lb of ethylene dichloride was exported from the United States in a recent year. The article states that "between 500 million and 550 million pounds of PVC could have been made from that ethylene dichloride." Compute the range of percentage yields of PVC from ethylene dichloride that is implied by these figures.

26. The complete hydrogenation of natural rubber (the addition of H_2 to all double bonds) gives a product that is indistinguishable from the product of the complete hydrogenation of gutta-percha. Explain how this strengthens the conclusion that these two substances are isomers of each other.

27. A reducing solution breaks S—S bonds in proteins, whereas an oxidizing solution allows them to re-form. Discuss how such solutions might be used to carry out the curling of hair.

28. L-Sucrose tastes sweet, but it is not metabolized. It has been suggested as a potential nonnutritive sweetener. Draw the molecular structure of L-sucrose, using Figure 23.16b as a starting point.

29. Polypeptides are synthesized from a 50:50 mixture of L-alanine and D-alanine. How many different isomeric molecules containing 22 monomer units are possible?

30. An osmotic pressure measurement taken on a solution containing hemoglobin shows that the molar mass of that protein is approximately 65,000 g mol^{-1}. A chemical analysis shows it to contain 0.344% of iron by mass. How many iron atoms does each hemoglobin molecule contain?

* **31.** At very low pH, alanine is a diprotic acid that can be represented as $H_3N^+-CH(CH_3)-COOH$. The pK_a of the carboxyl group is 2.3, and the pK_a of the $-NH_3^+$ group is 9.7.

(a) At pH 7, what fraction of the amino acid molecules dissolved in an aqueous solution will have the form $H_3N^+-CH(CH_3)-COO^-$?

(b) What fraction of the molecules at this pH will have the form $H_2N-CH(CH_3)-COOH$?

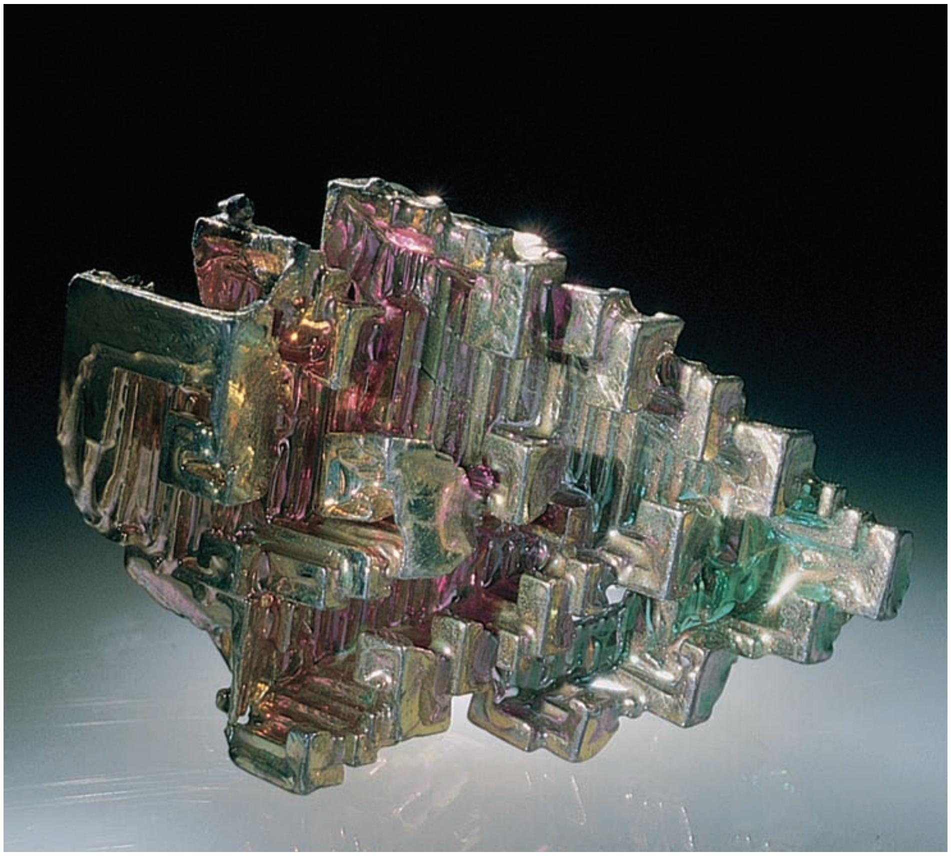
32. The sequence of bases in one strand of DNA reads ACTTGACCG. Write the sequence of bases in the complementary strand.

33. Nucleic acids are diesters of phosphoric acid. Esters are not usually acidic. Why are nucleic acids acidic, or is this name inappropriate?

34. The codons in the genetic code are sequences of three bases. Explain why sequences of only two bases could not be used to code for the 20 different amino acids commonly found in proteins.

35. The average distance between base pairs measured parallel to the axis of a double-helical DNA molecule is 3.4 angstroms. The average molecular weight of a pair of nucleotides is about 650 g mol^{-1}. What is the approximate length in millimeters of a single DNA molecule of molecular weight 2.8×10^9 g mol^{-1} (a value typical for the DNA of some bacteria)? About how many base pairs does this DNA contain?

Appendices



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A crystal of elemental bismuth.

APPENDIX A

Scientific Notation and Experimental Error

A.1 Scientific Notation

Very large and very small numbers are common in chemistry. Repeatedly writing such numbers in the ordinary way (for example, the important number 602,214,200,000,000,000,000,000) would be tedious and would engender errors. **Scientific notation** offers a better way. A number in scientific notation is expressed as a number from 1 to 10 multiplied by 10 raised to some power. Any number can be represented in this way, as the following examples show.

$$\begin{aligned} 643.8 &= 6.438 \times 10^{2} \\ -19{,}000{,}000 &= -1.9 \times 10^{7} \\ 0.0236 &= 2.36 \times 10^{-2} \\ 602{,}214{,}200{,}000{,}000{,}000{,}000{,}000 &= 6.022142 \times 10^{23} \end{aligned}$$

A simple rule of thumb is that the power to which 10 is raised is n if the decimal point is moved n places to the left and is $-n$ if the decimal is moved n places to the right.

When two or more numbers written in scientific notation are to be added or subtracted, they should first be expressed as multiples of the *same* power of 10:

$$\begin{array}{rcr} 6.431 \times 10^{4} & \longrightarrow & 6.431 \times 10^{4} \\ +2.1 \times 10^{2} & \longrightarrow & +0.021 \times 10^{4} \\ \underline{+3.67 \times 10^{3}} & \longrightarrow & \underline{+0.367 \times 10^{4}} \\ ? & & 6.819 \times 10^{4} \end{array}$$

When two numbers in scientific notation are multiplied, the coefficients are multiplied and then the powers of 10 are multiplied (by adding the exponents):

$$\begin{aligned} 1.38 \times 10^{-16} \times 8.80 \times 10^{3} &= (1.38 \times 8.80) \times 10^{(-16+3)} \\ &= 12.1 \times 10^{-13} = 1.21 \times 10^{-12} \end{aligned}$$

We divide one number by a second by dividing the coefficients and then multiplying by 10 raised to the first exponent minus the second (exponents are subtracted):

$$\begin{aligned} \frac{6.63 \times 10^{-27}}{2.34 \times 10^{-16}} &= \frac{6.63}{2.34} \times \frac{10^{-27}}{10^{-16}} \\ &= 2.83 \times 10^{[-27-(-16)]} = 2.83 \times 10^{-11} \end{aligned}$$

Any calculator or computer equipped to perform scientific and engineering calculations can accept and display numbers in scientific notation. It cannot determine whether the input has an error, however, or whether the answer makes sense. That is your responsibility! Develop the habit of mentally estimating the order of magnitude of the answer as a rough check on your calculator's result.

A.2 Experimental Error

Chemistry is an experimental science in which every quantitative measurement is subject to some degree of error. We can seek to reduce error by carrying out additional measurements or by changing our experimental apparatus, but we can never eliminate error altogether. It is important, therefore, to be able to assess the results of an experiment quantitatively to establish the limits of the experiment's validity. Errors are of two types: random (lack of precision) and systematic (lack of accuracy).

Precision and Random Errors

Precision refers to the degree of agreement in a collection of experimental results and is estimated by repeating the measurement under conditions as nearly identical as possible. If the conditions are truly identical, then differences among the trials are due to random error. As a specific example, consider some actual results of an early, important experiment by American physicist Robert Millikan in 1909, to measure the charge e on the electron. The experiment (discussed in greater detail in Chapter 1) involved a study of the motion of charged oil drops suspended in air in an electric field. Millikan made hundreds of measurements on many different oil drops, but we shall consider only a set of results for e found for one particular drop (Table A.1). The values he found ranged from 4.894 to 4.941×10^{-10} esu. What do we choose to report as the best estimate for e? The proper procedure is to first examine the data to see whether any of the results are especially far from the rest (a value above 5×10^{-10} esu would fall into this category). Such values are likely to result from some mistake in carrying out or reporting that particular measurement and therefore are excluded from further consideration (although there have been cases in science where just such exceptional results have led to significant breakthroughs). In Millikan's data, no such points should be excluded. To obtain our best estimate for e, we calculate the **mean,** or **average value,** by adding up the values found and dividing by the number of measurements. We can write the average value of any property after a series of N measurements $x_1, x_2, \ldots, x_N$ as

$$\bar{x} = \frac{1}{N}(x_1 + x_2 + \cdots + x_N) = \frac{1}{N}\sum_{i=1}^{N} x_i$$

where a capital Greek sigma (Σ) is introduced to indicate a summation of x_i over values of i from 1 to N. In the present case, this gives an average for e of 4.917×10^{-10} esu.

This average by itself does not convey any estimate of uncertainty. If all of the measurements had given results between 4.91×10^{-10} and 4.92×10^{-10} esu, the uncertainty would be less than if the results had ranged from 4×10^{-10} to 6×10^{-10} esu. Furthermore, an average of 100 measurements should have less uncertainty than an average of 5. How are these ideas made quantitative? A statistical

TABLE A.1

Measurement Number
e (10^{-10} esu)

1	2	3	4	5	6	7	8	9	10	11	12	13
4.915	4.920	4.937	4.923	4.931	4.936	4.941	4.902	4.927	4.900	4.904	4.897	4.894

From R. A. Millikan, *Phys. Rev.* 32:349, 1911. [1 esu = 3.3356×10^{-10} C] measure of the spread of data, called the **standard deviation** σ, is useful in this regard. It is given by the formula

$$\sigma = \sqrt{\frac{(x_1 - \overline{x})^2 + (x_2 - \overline{x})^2 + \cdots + (x_N - \overline{x})^2}{N - 1}}$$

$$= \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (x_i - \overline{x})^2}$$

The standard deviation is found by adding up the squares of the deviations of the individual data points from the average value $\overline{x}$, dividing by $N - 1$, and taking the square root. Table A.2 shows how σ is used quantitatively. A **confidence limit** is defined as

$$\text{confidence limit} = \pm \frac{t\sigma}{\sqrt{N}}$$

The table gives the factor t for various numbers of measurements, N, and for various levels of confidence.

For Millikan's data, $N = 13$ and $\sigma = 0.017 \times 10^{-10}$. For 95% confidence with 13 measurements, the table shows $t = 2.18$ and the confidence limit is

$$\text{confidence limit} = \pm \frac{(2.18)(0.017 \times 10^{-10})}{\sqrt{13}} = \pm 0.010 \times 10^{-10} \text{ esu}$$

Thus, a 95% probability exists that the *true* average (obtained by repeating the experiment under the same conditions an infinite number of times) will lie within $\pm 0.010 \times 10^{-10}$ esu of the average 4.917×10^{-10} esu. Within this 95% confidence level, our best estimate for e is written as

$$(4.917 \pm 0.010) \times 10^{-10} \text{ esu}$$

For other confidence levels and other numbers of measurements, the factor t and therefore the confidence limit change.

TABLE A.2

N	**Factor *t* for Confidence Interval of**			
(Number of Observations)	**80%**	**90%**	**95%**	**99%**
2	3.08	6.31	12.7	63.7
3	1.89	2.92	4.30	9.92
4	1.64	2.35	3.18	5.84
5	1.53	2.13	2.78	4.60
6	1.48	2.02	2.57	4.03
7	1.44	1.94	2.45	3.71
8	1.42	1.90	2.36	3.50
9	1.40	1.86	2.31	3.36
10	1.38	1.83	2.26	3.25
11	1.37	1.81	2.23	3.17
12	1.36	1.80	2.20	3.11
13	1.36	1.78	2.18	3.06
14	1.35	1.77	2.16	3.01
15	1.34	1.76	2.14	2.98
∞	1.29	1.64	1.96	2.58

Accuracy and Systematic Errors

The charge e on the electron has been measured by several different techniques since Millikan's day. The current best estimate for e is

$$\begin{aligned} e &= (4.80320775 \pm 0.0000015) \times 10^{-10} \text{ esu} \\ &= (1.60217646 \pm 0.00000049) \times 10^{-19} \text{ C} \end{aligned}$$

This value lies outside the range of uncertainty we estimated from Millikan's original data. In fact, it lies well below the smallest of the 13 measurements of e. Why?

To understand this discrepancy, we need to remember that there is a second source of error in any experiment: *systematic* error that causes a shift in the measured values from the true value and reduces the **accuracy** of the result. By making more measurements, we can reduce the uncertainty due to *random* errors and improve the *precision* of our result; however, if systematic errors are present, the average value will continue to deviate from the true value. Such systematic errors may result from a miscalibration of the experimental apparatus or from a fundamental inadequacy in the technique for measuring a property. In the case of Millikan's experiment, the then-accepted value for the viscosity of air (used in calculating the charge e) was subsequently found to be wrong. This caused his results to be systematically too high.

Error thus arises from two sources. Lack of precision (random errors) can be estimated by a statistical analysis of a series of measurements. Lack of accuracy (systematic errors) is much more problematic. If a systematic error is known to be present, we should do our best to correct for it before reporting the result. (For example, if our apparatus has not been calibrated correctly, it should be recalibrated.) The problem is that systematic errors of which we have no knowledge may be present. In this case the experiment should be repeated with different apparatus to eliminate the systematic error caused by a particular piece of equipment; better still, a different and independent way to measure the property might be devised. Only after enough independent experimental data are available can we be convinced of the accuracy of a result—that is, how closely it approximates the true result.

A.3 Significant Figures

The number of **significant figures** is the number of digits used to express a measured or calculated quantity, excluding zeros that may precede the first nonzero digit. Suppose the mass of a sample of sodium chloride is measured to be 8.241 g and the uncertainty is estimated to be ±0.001 g. The mass is said to be given to four significant figures because we are confident of the first three digits (8, 2, 4) and the uncertainty appears in the fourth (1), which nevertheless is still significant. Writing additional digits beyond the 1 would not be justified, however, unless the accuracy of the weighing could be improved. When we record a volume as 22.4 L, we imply that the uncertainty in the measurement is in the last digit written ($V = 22.4 \pm 0.3$ L, for example). A volume written as 22.43 L, on the other hand, implies that the uncertainty is far less and appears only in the fourth significant figure.

In the same way, writing 20.000 m is quite different from writing 20.0 m. The second measurement (with three significant figures) could easily be made with a common meterstick. The first (with five significant figures) would require a more precise method. We should avoid reporting results such as "700 m," however, because the two trailing zeros may or may not be significant. The uncertainty in the measurement could be of order ±1 m or ±10 m or perhaps ±100 m; it is impossible to tell which without further information. To avoid this ambiguity, we can write such measurements using the scientific notation described in Section A.1. The measurement “700 m” translates into any of the following:

7.00×10^2 m Three significant figures

7.0×10^2 m Two significant figures

7×10^2 m One significant figure

Frequently, it is necessary to combine several different experimental measurements to obtain a final result. Some operations involve addition or subtraction, and others entail multiplication or division. These operations affect the number of significant figures that should be retained in the calculated result. Suppose, for example, that a weighed sample of 8.241 g of sodium chloride is dissolved in 160.1 g of water. What will be the mass of the solution that results? It is tempting to simply write $160.1 + 8.241 = 168.341$ g, but this is *not* correct. In saying that the mass of water is 160.1 g, we imply that there is some uncertainty about the number of tenths of a gram measured. This uncertainty must also apply to the sum of the masses, so the last two digits in the sum are not significant and should be **rounded off,** leaving 168.3 as the final result.

> *Following addition or subtraction, round off the result to the leftmost decimal place that contained an uncertain digit in the original numbers.*

Rounding off is a straightforward operation. It consists of first discarding the digits that are not significant and then adjusting the last remaining digit. If the first discarded digit is less than 5, the remaining digits are left as they are (for example, 168.341 is rounded down to 168.3 because the first discarded digit, 4, is less than 5). If the first discarded digit is greater than 5, or if it is equal to 5 and is followed by one or more nonzero digits, then the last digit is increased by 1 (for example, 168.364 and 168.3503 both become 168.4 when rounded off to four digits). Finally, if the first digit discarded is 5 and all subsequent digits are zeros, the last digit remaining is rounded to the nearest even digit (for example, both 168.35 and 168.45 would be rounded to 168.4). This last rule is chosen so that, on the average, as many numbers are rounded up as down. Other conventions are sometimes used.

In multiplication or division it is not the number of decimal places that matters (as in addition or subtraction) but the number of significant figures in the least precisely known quantity. Suppose, for example, the measured volume of a sample is 4.34 cm^3 and its mass is 8.241 g. The density, found by dividing the mass by the volume on a calculator, for example, is

$$\frac{8.241\ \text{g}}{4.34\ \text{cm}^3} = 1.89884\ldots\ \text{g cm}^{-3}$$

How many significant figures should we report? Because the volume is the less precisely known quantity (three significant figures as opposed to four for the mass), it controls the precision that may properly be reported in the answer. Only three significant figures are justified, so the result is rounded to 1.90 g cm^{-3}.

> *The number of significant figures in the result of a multiplication or division is the smallest of the numbers of significant figures used as input.*

It is best to carry out the arithmetical operations and *then* round the final answer to the correct number of significant figures, rather than round off the input data first. The difference is usually small, but this recommendation is nevertheless worth following. For example, the correct way to add the three distances 15 m, 6.6 m, and 12.6 m is

$$\begin{array}{r} 15\ \text{m} \\ +\ 6.6\ \text{m} \\ \underline{+12.6\ \text{m}} \\ 34.2\ \text{m} \end{array} \longrightarrow 34\ \text{m} \qquad \text{rather than} \qquad \begin{array}{rcr} 15\ \text{m} & \longrightarrow & 15\ \text{m} \\ 6.6\ \text{m} & \longrightarrow & 7\ \text{m} \\ 12.6\ \text{m} & \longrightarrow & \underline{13\ \text{m}} \\ & & 35\ \text{m} \end{array}$$

For the same reason, we frequently carry extra digits through the intermediate steps of a worked example and round off only for the final answer. If a calculation is done entirely on a scientific calculator or a computer, several extra digits are usually carried along automatically. Before the final answer is reported, however, it is important to round off to the proper number of significant figures.

Sometimes pure constants appear in expressions. In this case the accuracy of the result is determined by the accuracy of the other factors. The uncertainty in the volume of a sphere, $\frac{4}{3}\pi r^3$, depends only on the uncertainty in the radius r; 4 and 3 are pure constants (4.000 . . . and 3.000 . . . , respectively), and π can be given to as many significant figures (3.14159265 . . .) as are warranted by the radius.

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G.

Scientific Notation

1. Express the following in scientific notation.
- (a) 0.0000582
- (b) 402
- (c) 7.93
- (d) −6593.00
- (e) 0.002530
- (f) 1.47

2. Express the following in scientific notation.
- (a) 4579
- (b) −0.05020
- (c) 2134.560
- (d) 3.825
- (e) 0.0000450
- (f) 9.814

3. Convert the following from scientific notation to decimal form.
- (a) 5.37×10^{-4}
- (b) 9.390×10^{6}
- (c) -2.47×10^{-3}
- (d) 6.020×10^{-3}
- (e) 2×10^{4}

4. Convert the following from scientific notation to decimal form.
- (a) 3.333×10^{-3}
- (b) -1.20×10^{7}
- (c) 2.79×10^{-5}
- (d) 3×10^{1}
- (e) 6.700×10^{-2}

5. A certain chemical plant produces 7.46×10^{8} kg of polyethylene in one year. Express this amount in decimal form.

6. A microorganism contains 0.0000046 g of vanadium. Express this amount in scientific notation.

Experimental Error

7. A group of students took turns using a laboratory balance to weigh the water contained in a beaker. The results they reported were 111.42 g, 111.67 g, 111.21 g, 135.64 g, 111.02 g, 111.29 g, and 111.42 g.
- (a) Should any of the data be excluded before the average is calculated?
- (b) From the remaining measurements, calculate the average value of the mass of the water in the beaker.
- (c) Calculate the standard deviation σ and, from it, the 95% confidence limit.

8. By measuring the sides of a small box, a group of students made the following estimates for its volume: 544 cm^3, 590 cm^3, 523 cm^3, 560 cm^3, 519 cm^3, 570 cm^3, and 578 cm^3.
- (a) Should any of the data be excluded before the average is calculated?
- (b) Calculate the average value of the volume of the box from the remaining measurements.
- (c) Calculate the standard deviation σ and, from it, the 90% confidence limit.

9. Of the measurements in problems 7 and 8, which is more precise?

10. A more accurate determination of the mass in problem 7 (using a better balance) gives the value 104.67 g, and an accurate determination of the volume in problem 8 gives the value 553 cm^3. Which of the two measurements in problems 7 and 8 is more accurate, in the sense of having the smaller systematic error relative to the actual value?

Significant Figures

11. State the number of significant figures in each of the following measurements.
- (a) 13.604 L
- (b) −0.00345°C
- (c) 340 lb
- (d) 3.40×10^{2} miles
- (e) 6.248×10^{-27} J

12. State the number of significant figures in each of the following measurements.
(a) -0.0025 in
(b) 7000 g
(c) 143.7902 s
(d) 2.670×10^{7} Pa
(e) 2.05×10^{-19} J

13. Round off each of the measurements in problem 11 to two significant figures.

14. Round off each of the measurements in problem 12 to two significant figures.

15. Round off the measured number 2,997,215.548 to nine significant digits.

16. Round off the measured number in problem 15 to eight, seven, six, five, four, three, two, and one significant digits.

17. Express the results of the following additions and subtractions to the proper number of significant figures. All of the numbers are measured quantities.
(a) $67.314 + 8.63 - 243.198 =$
(b) $4.31 + 64 + 7.19 =$
(c) $3.1256 \times 10^{15} - 4.631 \times 10^{13} =$
(d) $2.41 \times 10^{-26} - 7.83 \times 10^{-25} =$

18. Express the results of the following additions and subtractions to the proper number of significant figures. All of the numbers are measured quantities.
(a) $245.876 + 4.65 + 0.3678 =$
(b) $798.36 - 1005.7 + 129.652 =$
(c) $7.98 \times 10^{17} + 6.472 \times 10^{19} =$
(d) $(4.32 \times 10^{-15}) + (6.257 \times 10^{-14}) - (2.136 \times 10^{-13}) =$

19. Express the results of the following multiplications and divisions to the proper number of significant figures. All of the numbers are measured quantities.
(a) $\dfrac{-72.415}{8.62} =$
(b) $52.814 \times 0.00279 =$
(c) $(7.023 \times 10^{14}) \times (4.62 \times 10^{-27}) =$
(d) $\dfrac{4.3 \times 10^{-12}}{9.632 \times 10^{-26}} =$

20. Express the results of the following multiplications and divisions to the proper number of significant figures. All of the numbers are measured quantities.
(a) $129.587 \times 32.33 =$
(b) $\dfrac{4.7791}{3.21 \times 5.793} =$
(c) $\dfrac{10566.9}{3.584 \times 10^{29}} =$
(d) $(5.247 \times 10^{13}) \times (1.3 \times 10^{-17}) =$

21. Compute the area of a triangle (according to the formula $A = \frac{1}{2}ba$) if its base and altitude are measured to equal 42.07 cm and 16.0 cm, respectively. Justify the number of significant figures in the answer.

22. An inch is defined as exactly 2.54 cm. The length of a table is measured as 505.16 cm. Compute the length of the table in inches. Justify the number of significant figures in the answer.

APPENDIX B

SI Units, Unit Conversions, and Physics for General Chemistry

This appendix reviews essential concepts of physics, as well as systems of units of measure, essential for work in general chemistry.

B.1 SI Units and Unit Conversions

Scientific work requires measurement of quantities or properties observed in the laboratory. Results are expressed not as pure numbers but rather as **dimensions** that reflect the nature of the property under study. For example, mass, time, length, area, volume, energy, and temperature are fundamentally distinct quantities, each of which is characterized by its unique dimension. The magnitude of each dimensioned quantity can be expressed in various **units** (for example, feet or centimeters for length). Several systems of units are available for use, and facility at conversion among them is essential for scientific work. Over the course of history, different countries evolved different sets of units to express length, mass, and many other physical dimensions. Gradually, these diverse sets of units are being replaced by international standards that facilitate comparison of measurements made in different localities and that help avoid complications and confusion. The unified system of units recommended by international agreement is called SI, which stands for "Système International d'Unités," or the International System of Units. In this section we outline the use of SI units and discuss interconversions with other systems of units.

The SI uses seven **base units,** which are listed in Table B.1. All other units can be written as combinations of the base units. In writing the units for a measurement, we abbreviate them (see Table B.1), and we use exponential notation to denote the power to which a unit is raised; a minus sign appears in the exponent

TABLE B.1 Base Units in the International System of Units

Quantity	Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Temperature	kelvin	K
Number of moles (of substance)	mole	mol
Electric current	ampere	A
Luminous intensity	candela	cd

TABLE B.2 Derived Units in SI

Quantity	Unit	Symbol	Definition
Energy	joule	J	kg m^2 s^{-2}
Force	newton	N	kg m s^{-2} = J m^{-1}
Power	watt	W	kg m^2 s^{-3} = J s^{-1}
Pressure	pascal	Pa	kg m^{-1} s^{-2} = N m^{-2}
Electric charge	coulomb	C	A s
Electric potential difference	volt	V	kg m^2 s^{-3} A^{-1} = J C^{-1}

when the unit is in the denominator. For example, velocity is a quantity with dimensions of length divided by time, so in SI it is expressed in meters per second, or m s^{-1}. Some derived units that are used frequently have special names. Energy, for example, is the product of mass and the square of the velocity. Therefore, it is measured in units of kilogram square meters per square seconds (kg m^2 s^{-2}), and 1 kg m^2 s^{-2} is called a *joule*. Other derived units, such as the pascal for measuring pressure, appear in Table B.2. Although these names provide a useful shorthand, it is important to remember their meanings in terms of the base units.

Because scientists work on scales ranging from the microscopic to the astronomical, there is a tremendous range in the magnitudes of measured quantities. Consequently, a set of **prefixes** has been incorporated into the International System of Units to simplify the description of small and large quantities (Table B.3). The prefixes specify various powers of 10 times the base and derived units. Some of them are quite familiar in everyday use: the kilometer, for example, is 10^3 m. Others may sound less familiar—for instance, the femtosecond (1 fs = 10^{-15} s) or the gigapascal (1 GPa = 10^9 Pa).

In addition to base and derived SI units, several units that are not officially sanctioned are used in this book. The first is the liter (abbreviated L), a very convenient size for volume measurements in chemistry; a liter is 10^{-3} m^3, or 1 cubic decimeter (dm^3):

$$1\ \text{L} = 1\ \text{dm}^3 = 10^{-3}\ \text{m}^3 = 10^3\ \text{cm}^3$$

Second, we use the *angstrom* (abbreviated Å) as a unit of length for atoms and molecules:

$$1\ \text{Å} = 10^{-10}\ \text{m} = 100\ \text{pm} = 0.1\ \text{nm}$$

This unit is used simply because most atomic sizes and chemical bond lengths fall in the range of one to several angstroms, and the use of either picometers or nanometers is slightly awkward. Next, we use the *atmosphere* (abbreviated atm) as a unit of pressure. It is not a simple power of 10 times the SI unit of the pascal, but rather is defined as follows:

$$1\ \text{atm} = 101{,}325\ \text{Pa} = 0.101325\ \text{MPa}$$

TABLE B.3 Prefixes in SI

Fraction	Prefix	Symbol	Factor	Prefix	Symbol
10^{-1}	*deci-*	d	10	*deca-*	da
10^{-2}	*centi-*	c	10^2	*hecto-*	h
10^{-3}	*milli-*	m	10^3	*kilo-*	k
10^{-6}	*micro-*	μ	10^6	*mega-*	M
10^{-9}	*nano-*	n	10^9	*giga-*	G
10^{-12}	*pico-*	p	10^{12}	*tera-*	T
10^{-15}	*femto-*	f			
10^{-18}	*atto-*	a			

This unit is used because most chemistry procedures are carried out at pressures near atmospheric pressure, for which the pascal is too small a unit to be convenient. In addition, expressions for equilibrium constants (see Chapter 14) are simplified when pressures are expressed in atmospheres.

The non-SI temperature units require special mention. The two most important temperature scales in the United States are the Fahrenheit scale and the Celsius scale, which employ the Fahrenheit degree (°F) and the Celsius degree (°C), respectively. The *size* of the Celsius degree is the same as that of the SI temperature unit, the kelvin, but the two scales are shifted relative to each other by 273.15°C:

$$T_{\mathrm{K}} = \frac{1\ \mathrm{K}}{1^\circ\mathrm{C}}(t^\circ\mathrm{C}) + 273.15\ \mathrm{K}$$

The size of the degree Fahrenheit is $\frac{5}{9}$ the size of the Celsius degree. The two scales are related by

$$t^\circ\mathrm{C} = \frac{5^\circ\mathrm{C}}{9^\circ\mathrm{F}}(t^\circ\mathrm{F} - 32^\circ\mathrm{F}) \qquad \text{or} \qquad t^\circ\mathrm{F} = \frac{9^\circ\mathrm{F}}{5^\circ\mathrm{C}}(t^\circ\mathrm{C}) + 32^\circ\mathrm{F}$$

The advantage of a unified system of units is that if all the quantities in a calculation are expressed in SI units, the final result must come out in SI units. Nevertheless, it is important to become familiar with the ways in which units are interconverted because units other than SI base units often appear in calculations. The **unit conversion method** provides a systematic approach to this problem.

As a simple example, suppose the mass of a sample is measured to be 64.3 g. If this is to be used in a formula involving SI units, it should be converted to kilograms (the SI base unit of mass). To do this, we use the fact that 1 kg = 1000 g and write

$$\frac{64.3\ \mathrm{g}}{1000\ \mathrm{g\ kg^{-1}}} = 0.0643\ \mathrm{kg}$$

Note that this is, in effect, division by 1; because 1000 g = 1 kg, $1000\ \mathrm{g\ kg^{-1}} = 1$, and we cancel units between numerator and denominator to obtain the final result. This unit conversion could also be written as

$$64.3\ \mathrm{g}\left(\frac{1\ \mathrm{kg}}{1000\ \mathrm{g}}\right) = 0.0643\ \mathrm{kg}$$

In this book we use the more compact first version of the unit conversion. Instead of *dividing* by $1000\ \mathrm{g\ kg^{-1}}$, we can equally well *multiply* by $1 = 10^{-3}\ \mathrm{kg\ g^{-1}}$:

$$(64.3\ \mathrm{g})(10^{-3}\ \mathrm{kg\ g^{-1}}) = 0.0643\ \mathrm{kg}$$

Other unit conversions may involve more than just powers of 10, but they are equally easy to carry out. For example, to express 16.4 inches in meters, we use the fact that 1 inch = 0.0254 m (or $1 = 0.0254\ \mathrm{m\ inch^{-1}}$), so

$$(16.4\ \mathrm{inches})(0.0254\ \mathrm{m\ inch^{-1}}) = 0.417\ \mathrm{m}$$

More complicated combinations are possible. For example, to convert from liter-atmospheres to joules (the SI unit of energy), two separate unit conversions are used:

$$\begin{aligned}(1\ \mathrm{L\ atm})(10^{-3}\ \mathrm{m^3\ L^{-1}})(101{,}325\ \mathrm{Pa\ atm^{-1}}) &= 101.325\ \mathrm{kg\ m^2\ s^{-2}} \\ &= 101.325\ \mathrm{Pa\ m^3} = 101.325\ \mathrm{J}\end{aligned}$$

When doing chemical calculations, it is very important to write out units explicitly and cancel units in intermediate steps to obtain the correct units for the final result. This practice is a way of checking to make sure that units have not been incorrectly mixed without unit conversions or that an incorrect formula has not been used. If a result that is supposed to be a temperature comes out with units of $\mathrm{m^3\ s^{-2}}$, then a mistake has been made!

B.2 Background in Physics

Although physics and chemistry are distinct sciences with distinct objectives and methods of investigation, concepts from one can aid investigations in the other. Physical reasoning aids chemical understanding in cases where applied forces move chemical systems to new positions—or change their sizes and shapes—and change their energy. These energy changes can have chemical consequences, as shown in two specific examples. First, the total energy content of a system increases when the system is compressed by externally applied pressure. Second, when significant forces exist between molecules, the mutual energy of a pair of molecules changes as the molecules are pushed closer together. Intermolecular forces profoundly influence the organization of matter into solid, liquid, and gaseous states, as well as the effectiveness of molecular collisions in causing chemical reactions. Specific illustrations appear at many places in this book. This section reviews general aspects of motion, forces, and energy as background for these specific applications. For simplicity, we limit the discussion to a **point mass,** which is an object characterized only by its total mass m. We do not inquire into the internal structure of the object. In various contexts, we represent planets, projectiles, molecules, atoms, nuclei, or electrons by this model to predict their response to applied forces.

Describing the Motion of an Object

Our goal here is to find a precise way to describe how an object changes its location and how that change occurs at various rates. We need several definitions. First, we define the position of the object precisely by stating its **displacement** x from a selected reference point. For example, an automobile could be located 1.5 miles north of the intersection of Wilshire and Westwood boulevards in Los Angeles. The electron in a hydrogen atom could be located 5×10^{-11} m from the nucleus. Displacement has dimensions of length (L). The rate of change of location is given by the **average velocity** v, defined over the time interval t_1 to t_2 as $v = [x_2 - x_1]/[t_2 - t_1]$. Both the displacement and the average velocity are defined relative to the selected reference point and therefore possess direction as well as magnitude. The **average speed** s gives the magnitude of the average velocity but not its direction. For example, an automobile can have average velocity of 35 mph southbound from Wilshire and Westwood, while its average speed is 35 mph. Both velocity and speed have dimension of length per time (L t^{-1}). The **momentum** p of a body is defined as $p = mv$. The momentum indicates the ability of a moving body to exert impact on another body upon collision. For example, a slow-moving automobile “packs a bigger wallop” than a fast-moving bicycle. Momentum has dimensions of M L t^{-1}. The rate at which the velocity changes is given by the **acceleration** a, defined as $a = [v_2 - v_1]/[t_2 - t_1]$. Acceleration has direction as well as magnitude and has dimensions of L t^{-2}.

Forces Change the Motion of an Object

Force is defined as the agent that changes the motion of an object. This restatement of our daily experience that pushing or pulling an object causes it to move is the basis of Sir Isaac Newton’s first law of motion:

> *Every object persists in a state of rest or of uniform motion in a straight line unless compelled to change that state by forces impressed upon it.*

We determine the properties of a force experimentally in the laboratory by measuring the consequences of applying the force. Suppose we have arbitrarily selected a standard test object of known mass m_1. We apply a force F_1 and, by making the distance and time measurements described earlier, determine the acceleration $a_{1,1}$ imparted to the object by the force. Experience shows that a different force F_2 imparts different acceleration $a_{1,2}$ to the test object. Forces can be ranked by the magnitude of the acceleration they impart to the standard test object. Now suppose we choose a second test object of mass m_2. Applying the original force F_1 to this object produces acceleration $a_{2,1}$, which is different from the acceleration $a_{1,1}$ that it gave to the first test object. The results of such experiments are summarized in Newton's second law of motion:

> *The acceleration imparted to an object by an applied force is proportional to the magnitude of the force, parallel to the direction of the force, and inversely proportional to the mass of the object.*

In mathematical form this statement becomes

$$F = ma \quad \text{or} \quad a = F/m$$

This equation demonstrates that force must have dimensions of M L t^{-2}. In SI units, force is expressed in newtons (N).

One familiar example is the force caused by gravity at the surface of the earth. Measurements show this force produces a downward acceleration (toward the center of the earth) of constant magnitude 9.80665 m s^{-2}, conventionally denoted by g, the gravitational constant. The gravitational force exerted on a body of mass m is

$$F = mg$$

Another familiar example is the restoring force exerted on an object by a spring. In chemistry this is a useful model of the binding forces that keep atoms together in a chemical bond or near their "home" positions in a solid crystal. Imagine an object of mass m located on a smooth tabletop. The object is connected to one end of a coiled metallic spring; the other end of the spring is anchored to a post in the tabletop. At rest, the object is located at position x_0. Now suppose the object is pulled away from the post in a straight line to a new position x beyond x_0 so the spring is stretched. Measurements show that at the stretched position x the magnitude of the force exerted on the object by the spring is directly proportional to the displacement from the rest position:

$$|F| = K(x - x_0)$$

In the preceding equation, K is a constant whose magnitude must be determined empirically in each case studied. Clearly, this force is directed back toward the rest position, and when the object is released, the recoiling spring accelerates the object back toward the rest position. Because the displacement is directed *away* from the rest position and the restoring force is directed *toward* the rest position, we insert a minus sign in the equation:

$$F(x) = -K(x - x_0)$$

When studying the dependence of force on position, we must pay careful attention to how displacement is defined in each particular problem. The force and the acceleration at any point are parallel to each other, but the displacement (defined relative to some convenient origin of coordinates in each particular case) may point in a different direction. In applications concerned with the height of an object above the earth, the gravitational force is usually written as

$$F(y) = -mg$$

to emphasize that the vertical displacement y is positive and pointing away from the surface of the earth, while the gravitational force is clearly directed toward the earth.

Once a force has been determined, the motion of the object under that force can be predicted from Newton's second law. If a constant force (that is, a force with constant acceleration) is applied to an object initially at rest for a period of time starting at t_1 and ending at t_2, the velocity at t_2 is given by

$$v(t_2) = a(t_2 - t_1)$$

and the position at t_2 is given by

$$x(t_2) = x(t_1) + \tfrac{1}{2}a(t_2 - t_1)^2$$

If the force depends on position, predicting the motion is slightly more complicated and requires the use of calculus. We merely quote the results for the linear restoring force. Under this force, the object oscillates about the rest position x_0 with a period τ given by

$$\frac{1}{\tau} = \frac{1}{2\pi}\left(\frac{K}{m}\right)^{1/2}$$

The frequency ν of the oscillation (the number of cycles per unit time) is given by $\nu = \tau^{-1}$. If we represent the motion in terms of the angular frequency $\omega = 2\pi\nu$, which has dimensions radians s^{-1}, the position of the oscillating object is given by

$$x(t) - x_0 = A\cos(\omega t + \delta)$$

where the amplitude A and the phase factor δ are determined by the initial position and velocity of the object.

Forms of Energy

The concept of **energy** originated in the science of mechanics and was first defined as the capacity to perform work, that is, to move an object from one position to another. It is now understood that energy appears in many different forms, each of which can cause particular kinds of physical and chemical changes. From daily experience, we recognize the kinetic energy due to the speed of an onrushing automobile. To stop the automobile, its *kinetic energy* must be overcome by work performed by its brakes. Otherwise, the automobile will crash into other objects and expend its kinetic energy by deforming these objects, as well as itself. The *potential energy* of a mass of snow on a ski slope becomes the kinetic energy of an avalanche. The *electrical energy* stored in a battery can move objects by driving motors, or warm objects through electric heaters. The chemical energy stored in gasoline can move objects by powering an internal combustion engine. The *thermal energy* of hot steam can move objects by driving a steam engine.

Each of these forms of energy plays a role in chemistry, and each is described at the appropriate point in this textbook. Here we concentrate on the nature of potential and kinetic energy and their interconversion. The understanding we gain here is essential background for understanding these other forms of energy.

The **kinetic energy** of a moving object is defined by

$$\mathcal{T} = \frac{1}{2}mv^2$$

where m is the mass of the object and v is its speed. A stationary object has no kinetic energy. In the SI systems of units (see Appendix B.1), energy is expressed in joules (J). Thus, 0.5 joule is the kinetic energy of an object with mass 1 kg moving at a speed of 1 m s^{-1}. Experience shows that applying a force to a moving object changes the kinetic energy of the object. If the force is applied in the same direction as the velocity of the object, the kinetic energy is increased; if the force is opposed to the velocity, the kinetic energy is decreased.

Potential energy is the energy stored in an object due to its location relative to a specified reference position. Potential energy therefore depends explicitly on the position x of the object and is expressed as a mathematical function $V(x)$. The change in potential energy when an object is moved from position x_1 to position x_2 by a constant force is equal to the work done in moving the object:

$$\text{change in } V(x) = \text{force} \times \text{displacement} = \text{force} \times (x_2 - x_1)$$

To lift an object of mass m from the surface of the earth to the height h, some agency must perform work in the amount mgh against the downward-directed force of gravity, which has constant acceleration denoted by g. The change in potential energy is mgh. Potential energy is expressed in joules in the SI system of units.

Conservation of Energy

The science of mechanics deals with idealized motions of objects in which friction does not occur. The motions of an object interconvert its potential and kinetic energy subject to the restriction that their sum always remains constant. For example, consider a soccer ball rolling down the side of a steep gully at the edge of the playing field, and assume there is no friction between the ball and the surface on which it rolls. The ball rolls down one side, goes across the bottom, climbs partway up the opposite side, then stops and reverses direction. This pattern is repeated many times as the ball continues to oscillate back and forth across the bottom of the gully. On each downward leg of its journey, the ball loses potential energy and gains kinetic energy, but their sum remains constant. On each upward leg, the ball loses kinetic energy and gains potential energy, but their sum remains constant.

The description in the previous paragraph is clearly an idealization, because eventually the ball comes to rest at the bottom of the gully. In reality, the ball loses some of its kinetic energy through friction with the surface of the gully on each upward leg and on each downward leg of its journey. Both the ball and the gully surface become slightly warmer as a result. The energy lost from the purely mechanical motion is added to the *internal energy* of the ball and the gully surface. The total amount of energy has not changed; we have neither created nor destroyed energy in this process. Rather, we have identified a new mode of energy storage (called internal energy) to interpret the new effects beyond those explained by basic mechanics. Internal energy, heat, and friction are discussed in detail in Chapter 12 as part of the science of thermodynamics.

Similar arguments have extended the law of conservation of energy from the idealized motions of mechanics to include a broad variety of phenomena in which several different forms of energy are involved. This law is one of the securest building blocks in scientific reasoning. It provides the starting point for interpreting and relating a great variety of superficially different processes. In chemistry this law provides the foundation for studying complex processes in which kinetic, potential, electrical, chemical, and thermal energy are interconverted without net loss or gain.

Representing Energy Conservation by Potential Energy Curves

Consider again the soccer ball rolling down the walls of the gully. This process is shown schematically in Figure B.1, where the curve $V(x)$ suggests a "cross-sectional" sketch of the gully. The curve $V(x)$ actually represents the potential energy of the ball relative to its value at the bottom of the gully. The x coordinate locates the distance of the ball from the bottom of the gully to a position along its side. Suppose the ball is held in place at the position x_1. It possesses only potential energy, which we represent by the value E_1. If the ball is released, it falls down the slope and passes across the bottom, where its potential energy is zero and its kinetic energy is E_1. It then climbs the opposite side until it rises to position $-x_1$, where its kinetic energy is zero. The ball promptly reverses direction and retraces its path back to position x_1, where its total energy E_1 is all potential energy.

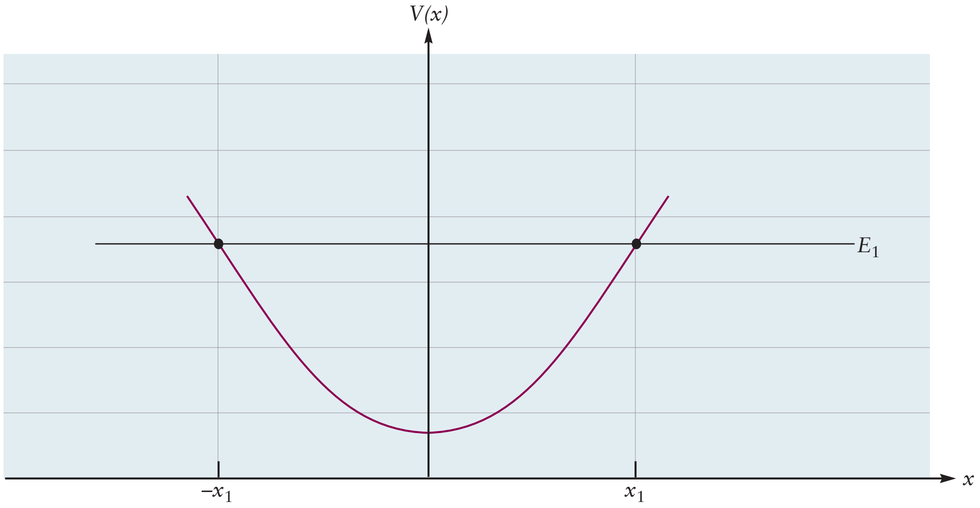

FIGURE B.1 Sketch of the potential energy of a soccer ball rolling down the sides of a gully. The ball is released at position x_1 with total energy E_1. In idealized motion, it continues to oscillate back and forth across the bottom of the gully. The net force on the ball is always in the direction in which the potential energy has negative slope. In real systems there is sufficient friction between the ball and the gully to bring the ball to rest at the bottom of the gully.

Potential Energy Curves, Force, and Stability

One very important application of the potential energy function in this textbook is to provide a way to qualitatively predict the motion of an object without solving Newton's second law. The method determines the direction of the force applied to an object from knowledge of the potential energy curve as shown in Figure B.1. In preparation for this method, let's examine the potential energy curves for some familiar forces.

The value of the potential energy at a general point x is always stated relative to its value at a specially selected reference point x_0. The value $V(x_0)$ is a constant and is usually assigned the value zero, and the point x_0 is frequently selected as the origin of coordinates for specifying the location of the object.

In the presence of a particular force F, the potential energy of the object at x is defined as the work required to move the object to x from the reference position x_0. Since the work done by a constant force in moving an object is defined as (force) × (displacement), the definition of potential energy in mathematical terms is

$$V(x) - V(x_0) = (F)(x - x_0)$$

Note carefully that the displacement referred to in the definition of potential energy starts at x_0 and ends at x. For example, the potential energy of an object of mass m at height h above the surface of the earth is the work done by a force $+mg$ opposing gravity in lifting the object from h_0 to h:

$$\begin{aligned} V(h) - V(h_0) &= mg(h - h_0) \\ &= mgh - mgh_0 \\ &= mgh \end{aligned}$$

where the value $V(h_0)$ has been set to zero. For a variable force, the definition of potential energy becomes slightly more complicated and requires explicit use of calculus. The potential energy for the linear restoring force is

$$V(x) = \tfrac{1}{2} K(x)^2$$

where the value $V(x_0)$ has been set to 0 and x_0 has been selected as the origin of coordinates.

It is instructive to plot these two potential energy functions as graphs (see Appendix C). The gravitational potential energy function is a straight line through the origin with slope mg, while the potential energy function for the linear restoring force is a parabola. In each case the potential energy of the object increases as the distance from the reference point x_0 increases.

Knowledge of the potential energy curve as a function of position lets us predict the net force on the object at each position. From either side, the force is directed toward the bottom; the force is always in the direction in which the slope of the potential energy curve is negative. From the definition of potential energy stated earlier, it can be shown that

$$\text{force} = -(\text{slope of PE})$$

The net force drives the object toward the position where the potential energy is a minimum and its slope is zero. For both the gravitational force and the linear restoring force, the object experiences negative forces that attract it back toward the center of force. In general, we identify **attractive forces** as those that correspond to positive slope of the potential energy curve; **repulsive forces** operate in regions where the slope of the potential energy curve is negative.

The minimum of the potential energy curve shown in Figure B.1 is called a point of **stable equilibrium** because the net force (that is, the slope of the potential energy curve) at that point is zero. As the ball tries to climb the wall on either side of the minimum, the restoring force always drives it back toward this position of stable equilibrium. This qualitative interpretation predicts that the ball will oscillate about the equilibrium position, as predicated by the exact solution to Newton's second law quoted earlier.

We use similar potential energy diagrams to represent the interaction between a pair of objects, such as Earth–moon, Earth–Mars, electron–nucleus, electron–electron, nucleus–nucleus, atom–atom, or molecule–molecule. We construct such diagrams at several points in this textbook and use them to interpret the relative motions of the pair of objects. These methods are extremely important in describing the formation of chemical bonds, the states of matter, and the role of molecular collisions in chemical reactions.

Electrical Forces

The concepts summarized so far in this section also are used to describe the mutual interactions and the motions of electrically charged particles. The only new features are to identify the force that represents electrical interactions and to obtain the corresponding potential energy function. Positive and negative charges and the electrical forces between them were first quantified by Charles Coulomb late in the 18th century. In his honor the unit of charge in SI units is the **coulomb** (C). Electrical charge is fundamentally quantized in units of the charge carried by a single electron e, which is equal to 1.60218×10^{-19} C. The coulomb is thus an inconveniently large unit for chemical reasoning. Nonetheless, for consistency and for quantitative accuracy, physical equations involving charge use SI units.

Suppose a charge of magnitude q_1 is held at the origin of coordinates and another charge of magnitude q_2 is brought near it, at the distance r from the origin. The magnitude of the acceleration imparted to the charge q_2 by the charge q_1 fixed at the origin can be determined as described earlier for uncharged objects. From such measurements, Coulomb determined that the magnitude of the force was directly proportional to the magnitudes of the two charges and inversely proportional to the distance between them:

$$F \propto \frac{q_1 q_2}{r^2}$$

The radial displacement variable r has its origin at the same location as charge q_1, and its value increases in the outward direction. If the charges have the same sign, the acceleration pushes them apart in the same direction as r. Consequently, the force between charges is **repulsive** and defined to be **positive.** If the charges have opposite signs, the acceleration pulls them together in the direction opposite to the displacement variable r. In this case the force between charges is **attractive** and defined to be **negative.** It is instructive to sketch the results graphically in these two cases. The quantitative form of Coulomb's law with force expressed in newtons (N) and charge in coulombs (C) is

$$F = \frac{q_1 q_2}{4\pi \epsilon_0 r^2}$$

where ε_0, called the permittivity of the vacuum, is a constant with value $8.854 \times 10^{-12}\ \mathrm{C^2\ J^{-1}\ m^{-1}}$. In this and related equations, the symbol q for each charge represents the magnitude and carries implicitly the sign of the charge.

The **Coulomb potential energy** corresponding to this force is

$$V(r) = \frac{q_1 q_2}{4\pi \epsilon_0 r}$$

Note that the force varies as r^{-2} while the potential energy varies as r^{-1}. Note also that if the charges have the same sign, the potential energy is positive and repulsive; if the charges have opposite sign, the potential energy is negative and attractive. If we know the potential energy curve between two charged particles, we can predict the direction of their relative motion.

The Coulomb potential energy function holds great importance in chemistry for examining the structure of atoms and molecules. In 1912, Ernest Rutherford proposed that an atom of atomic number Z comprises a dense, central nucleus of positive charge with magnitude Ze surrounded by a total of Z individual electrons moving around the nucleus. Thus, each individual electron has a potential energy of interaction with the nucleus given by

$$V(r) = -\frac{Ze^2}{4\pi \epsilon_0 r}$$

which is clearly negative and attractive. Each electron has a potential energy of interaction with every other electron in the atom given by

$$V(r) = \frac{e^2}{4\pi \epsilon_0 r}$$

which is clearly positive and repulsive. Rutherford's model of the atom, firmly based on experimental results, was completely at odds with the physical theories of the day. Attempts to reconcile these results with theory led to the development of the new theory called quantum mechanics.

Circular Motion and Angular Momentum

An object executing uniform circular motion about a point (for example, a ball on the end of a rope being swung in circular motion) is described by position, velocity, speed, momentum, and force, just as defined earlier for objects in linear motion. It is most convenient to describe this motion in polar coordinates r and θ, which represent, respectively, the distance of the object from the center and its angular displacement from the x-axis in ordinary cartesian coordinates. Because r is constant for circular motion, the motion variables depend directly on θ. The angular velocity during the time interval from t_1 to t_2 is given by

$$\omega = \frac{\theta_2 - \theta_1}{t_2 - t_1}$$

and the angular acceleration is given by

$$\alpha = \frac{\omega_2 - \omega_1}{t_2 - t_1}$$

In linear motion, we are concerned with the momentum $p = mv$ of an object as it heads toward a particular point; the linear momentum measures the impact that the object can transfer in a collision as it arrives at the point. To extend this concept to circular motion, we define the **angular momentum** of an object as it revolves around a point as $L = mvr$. This is in effect the *moment* of the linear momentum over the distance r, and it is a measure of the torque felt by the object as it executes angular motion. The angular momentum of an electron around a nucleus is a crucial feature of atomic structure, which is discussed in Chapter 5.

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G.

SI Units and Unit Conversions

1. Rewrite the following in scientific notation, using only the base units of Table B.1, without prefixes.
(a) 65.2 nanograms
(b) 88 picoseconds
(c) 5.4 terawatts
(d) 17 kilovolts

2. Rewrite the following in scientific notation, using only the base units of Table B.1, without prefixes.
(a) 66 μK
(b) 15.9 MJ
(c) 0.13 mg
(d) 62 GPa

3. Express the following temperatures in degrees Celsius.
(a) 9001°F
(b) 98.6°F (the normal body temperature of human beings)
(c) 20°F above the boiling point of water at 1 atm pressure
(d) −40°F

4. Express the following temperatures in degrees Fahrenheit.
(a) 5000°C
(b) 40.0°C
(c) 212°C
(d) −40°C

5. Express the temperatures given in problem 3 in kelvins.

6. Express the temperatures given in problem 4 in kelvins.

7. Express the following in SI units, either base or derived.
(a) 55.0 miles per hour (1 mile = 1609.344 m)
(b) 1.15 g cm^{-3}
(c) 1.6×10^{-19} C Å
(d) 0.15 mol L^{-1}
(e) 5.7×10^{3} L atm day^{-1}

8. Express the following in SI units, either base or derived.
(a) 67.3 atm
(b) 1.0×10^{4} V cm^{-1}
(c) 7.4 Å year^{-1}
(d) 22.4 L mol^{-1}
(e) 14.7 lb inch^{-2} (1 inch = 2.54 cm; 1 lb = 453.59 g)

9. The kilowatt-hour (kWh) is a common unit in measurements of the consumption of electricity. What is the conversion factor between the kilowatt-hour and the joule? Express 15.3 kWh in joules.

10. A car's rate of fuel consumption is often measured in miles per gallon (mpg). Determine the conversion factor between miles per gallon and the SI unit of meters per cubic decimeter (1 gallon = 3.785 dm^3, and 1 mile = 1609.344 m). Express 30.0 mpg in SI units.

11. A certain V-8 engine has a displacement of 404 in^3. Express this volume in cubic centimeters (cm^3) and in liters.

12. Light travels in a vacuum at a speed of 3.00×10^{8} m s^{-1}.
(a) Convert this speed to miles per second.
(b) Express this speed in furlongs per fortnight, a little-used unit of speed. (A furlong, a distance used in horse racing, is 660 ft; a fortnight is exactly 2 weeks.)

The Concept of Energy: Forms, Measurements, and Conservation

13. After being spiked, a volleyball travels with speed near 100 miles per hour. Calculate the kinetic energy of the volleyball. The mass of a volleyball is 0.270 kg.

14. The fastball of a famous pitcher in the National League has been clocked in excess of 95 mph. Calculate the work done by the pitcher in accelerating the ball to that speed. The mass of a baseball is 0.145 kg.

15. A tennis ball weighs approximately 2 ounces on a postage scale. A student practices his serve against the wall of the chemistry building, and the ball achieves the speed of 98 miles per hour. Calculate the kinetic energy of the ball after the serve. How much work is done on the chemistry building in one collision?

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APPENDIX C

Mathematics for General Chemistry

Mathematics is an essential tool in chemistry. This appendix reviews some of the most important mathematical techniques for general chemistry.

C.1 Using Graphs

In many situations in science, we are interested in how one quantity (measured or predicted) depends on another quantity. The position of a moving car depends on the time, for example, or the pressure of a gas depends on the volume of the gas at a given temperature. A very useful way to show such a relation is through a **graph,** in which one quantity is plotted against another.

The usual convention in drawing graphs is to use the horizontal axis for the variable over which we have control and use the vertical axis for the measured or calculated quantity. After a series of measurements, the points on the graph frequently lie along a recognizable curve, and that curve can be drawn through the points. Because any experimental measurement involves some degree of uncertainty, there will be some scatter in the points, so there is no purpose in drawing a curve that passes precisely through every measured point. If there is a relation between the quantities measured, however, the points will display a systematic trend and a curve can be drawn that represents that trend.

The curves plotted on graphs can have many shapes. The simplest and most important shape is a straight line. A straight line is a graph of a relation such as

$$y = 4x + 7$$

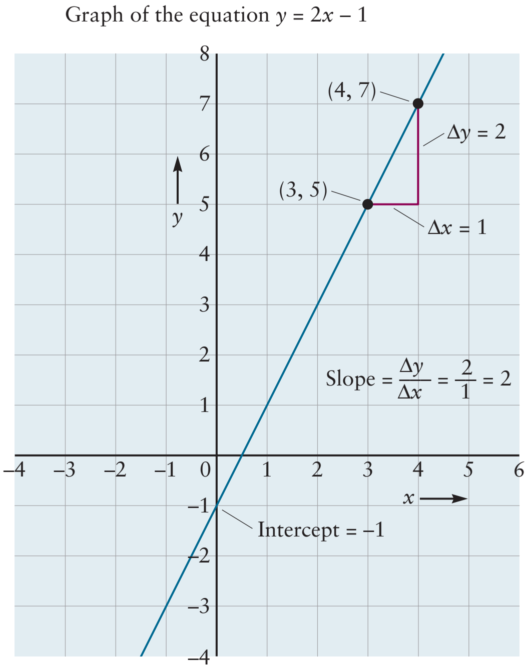
or, more generally,

$$y = mx + b$$

where the variable y is plotted along the vertical axis and the variable x along the horizontal axis (Fig. C.1). The quantity m is the **slope** of the line that is plotted, and b is the **intercept**—the point at which the line crosses the y axis. This can be demonstrated by setting x equal to 0 and noting that y is then equal to b. The slope is a measure of the steepness of the line; the greater the value of m, the steeper the line. If the line goes up and to the right, the slope is positive; if it goes down and to the right, the slope is negative.

The slope of a line can be determined from the coordinates of two points on the line. Suppose, for example, that when $x = 3$, $y = 5$, and when $x = 4$, $y = 7$. These two points can be written in shorthand notation as (3, 5) and (4, 7). The

FIGURE C.1 A straight-line, or linear, relationship between two experimental quantities is a very desirable result because it is easy to graph and easy to represent mathematically. The equation of this straight line ($y = 2x - 1$) fits the general form $y = mx + b$. The line's y intercept is -1 and its slope is 2.



slope of the line is then defined as the "rise over the run"—the change in the y coordinate divided by the change in the x coordinate:

$$\text{slope} = m = \frac{\Delta y}{\Delta x} = \frac{7 - 5}{4 - 3} = \frac{2}{1} = 2$$

The symbol Δ (capital Greek delta) indicates the change in a quantity—the final value minus the initial value. In chemistry, if the two quantities being graphed have dimensions, the slope has dimensions as well. If a graph of distance traveled (in meters) against time (in seconds) is a straight line, its slope has dimensions of meters per second (m s^{-1}).

C.2 Solution of Algebraic Equations

In chemistry it is often necessary to solve an algebraic equation for an unknown quantity, such as a concentration or a partial pressure in an equilibrium-constant expression. Let us represent the unknown quantity with the symbol x. If the equation is linear, the method of solution is straightforward:

$$5x + 9 = 0$$

$$5x = -9$$

$$x = -\frac{9}{5}$$

or, more generally, if $ax + b = 0$, then $x = -b/a$.

Nonlinear equations are of many kinds. One of the most common in chemistry is the quadratic equation, which can always be rearranged into the form

$$ax^2 + bx + c = 0$$

where each of the constants (a, b, and c) may be positive, negative, or 0. The two solutions to a quadratic equation are given by the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

As an example, suppose that the equation

$$x = 3 + \frac{7}{x}$$

arises in a chemistry problem. Multiplying by x and rearranging the terms gives

$$x^2 - 3x - 7 = 0$$

Inserting $a = 1$, $b = -3$, and $c = -7$ into the quadratic formula gives

$$x = \frac{-(-3) \pm \sqrt{(-3)^2 - 4(1)(-7)}}{2} = \frac{3 \pm \sqrt{9 + 28}}{2} = \frac{3 \pm \sqrt{37}}{2}$$

The two roots of the equation are

$$x = 4.5414 \qquad \text{and} \qquad x = -1.5414$$

In a chemistry problem, the choice of the proper root can frequently be made on physical grounds. If x corresponds to a concentration, for example, the negative root is unphysical and can be discarded.

The solution of cubic or higher order algebraic equations (or more complicated equations involving sines, cosines, logarithms, or exponentials) becomes more difficult, and approximate or numerical methods must be used. As an illustration, consider the equation

$$x^2\left(\frac{2.00 + x}{3.00 - x}\right) = 1.00 \times 10^{-6}$$

If x is assumed to be small relative to both 2.00 and 3.00, we obtain the simpler approximate equation

$$x^2\left(\frac{2.00}{3.00}\right) \approx 1.00 \times 10^{-6}$$

which leads to the roots $x = \pm 0.00122$. We immediately confirm that the solutions obtained in this way *are* small compared with 2.00 (and 3.00) and that our approximation was a good one. When a quantity (x in this case) is added to or subtracted from a larger quantity in a complicated equation, it is usually worthwhile, in solving the equation, to simply neglect the occurrence of the small quantity. Note that this tactic works only for addition and subtraction, never for multiplication or division.

Suppose now that the equation is changed to

$$x^2\left(\frac{2.00 + x}{3.00 - x}\right) = 1.00 \times 10^{-2}$$

In this case the equation that comes from neglecting x compared with 2.00 and 3.00 is

$$x^2\left(\frac{2.00}{3.00}\right) \approx 1.00 \times 10^{-2}$$

which is solved by $x \approx \pm 0.122$. The number 0.122 is smaller than 2.00 and 3.00, but not so small that it can be ignored. In this case more precise results can be obtained by **iteration.** Let us simply add and subtract the approximate positive root $x \approx +0.122$ as specified inside the parentheses and solve again for x:

$$x^2\left(\frac{2.00 + 0.122}{3.00 - 0.122}\right) = 1.00 \times 10^{-2}$$

$$x = 0.116$$

This new value can again be inserted into the original equation and the process repeated:

$$x^2\left(\frac{2.00 + 0.116}{3.00 - 0.116}\right) = 1.00 \times 10^{-2}$$

$$x = 0.117$$

Once the successive values of x agree to within the desired accuracy, the iteration can be stopped. Another root of the equation is obtained in a similar fashion if the iterative procedure starts with $x = -0.122$.

In some cases iteration fails. Suppose, for example, we have the equation

$$x^2\left(\frac{2.00 + x}{3.00 - x}\right) = 10.0$$

There is no particular reason to believe that x should be small compared with 2.00 or 3.00, but if we nevertheless assume that it is, we find $x = \pm\sqrt{15} = \pm 3.873$. Putting $x = +3.873$ back in for an iterative cycle leads to the equation

$$x^2 = -1.49$$

which has no real solutions. Starting with $x = -3.873$ succeeds no better; it gives

$$x^2 = -36.7$$

One way to overcome these difficulties is to solve the original equation graphically. We plot the left side of the equation against x and see at which values it becomes equal to 10 (the right side). We might initially calculate

x	$x^2\left(\frac{2.00 + x}{3.00 - x}\right)$
0	0
1	1.5
2	16

We observe that for $x = 1$ the left side is less than 10, whereas for $x = 2$ it is greater than 10. Somewhere in between there must be an x for which the left side is *equal to* 10. We can pinpoint it by selecting values of x between 1 and 2; if the left side is less than 10, x should be increased, and if it is greater than 10, x should be decreased.

x	$x^2\left(\frac{2.00 + x}{3.00 - x}\right)$
1.5	5.25
Increase to 1.8	10.26
Decrease to 1.75	9.19
Increase to 1.79	10.04

Thus, 1.79 is quite close to a solution of the equation. Improved values are easily obtained by further adjustments of this type.

C.3 Powers and Logarithms

Raising a number to a power and the inverse operation, taking a logarithm, are important in many chemical problems. Although the ready availability of electronic calculators makes the mechanical execution of these operations quite routine, it remains important to understand what is involved in such "special functions."

The mathematical expression 10^4 implies multiplying 10 by itself 4 times to give 10,000. Ten, or any other number, when raised to the power 0 always gives 1:

$$10^0 = 1$$

Negative powers of 10 give numbers less than 1 and are equivalent to raising 10 to the corresponding *positive* power and then taking the reciprocal:

$$10^{-3} = 1/10^3 = 0.001$$

We can extend the idea of raising to a power to include powers that are not whole numbers. For example, raising to the power $\frac{1}{2}$ (or 0.5) is the same as taking the square root:

$$10^{0.5} = \sqrt{10} = 3.1623\ldots$$

Scientific calculators have a 10^x (or INV LOG) key that can be used for calculating powers of 10 in cases where the power is not a whole number.

Numbers other than 10 can be raised to powers, as well; these numbers are referred to as **bases.** Many calculators have a y^x key that lets any positive number y be raised to any power x. One of the most important bases in scientific problems is the transcendental number called e (2.7182818 . . .). The e^x (or INV LN) key on a calculator is used to raise e to any power x. The quantity e^x also denoted as $\exp(x)$, is called the **exponential** of x. A key property of powers is that a base raised to the sum of two powers is equivalent to the product of the base raised separately to these powers. Thus, we can write

$$10^{21+6} = 10^{21} \times 10^6 = 10^{27}$$

The same type of relationship holds for any base, including e.

Logarithms also occur frequently in chemistry problems. The logarithm of a number is the exponent to which some base has to be raised to obtain the number. The base is almost always either 10 or the transcendental number e. Thus,

$$B^a = n \qquad \text{and} \qquad \log_B n = a$$

where a is the logarithm, B is the base, and n is the number.

Common logarithms are base-10 logarithms; that is, they are powers to which 10 has to be raised in order to give the number. For example, $10^3 = 1000$, so $\log_{10} 1000 = 3$. We shall frequently omit the 10 when showing common logarithms and write this equation as $\log 1000 = 3$. Only the logarithms of 1, 10, 100, 1000, and so on are whole numbers; the logarithms of other numbers are decimal fractions. The decimal point in a logarithm divides it into two parts. To the left of the decimal point is the *characteristic;* to the right is the *mantissa*. Thus, the logarithm in the equation

$$\log (7.310 \times 10^3) = 3.8639$$

has a characteristic of 3 and a mantissa of 0.8639. As may be verified with a calculator, the base-10 logarithm of the much larger (but closely related) number 7.310×10^{23} is 23.8639. As this case illustrates, the characteristic is determined solely by the location of the decimal point in the number and not by the number's precision, so it is *not* included when counting significant figures. The mantissa should be written with as many significant figures as the original number.

A logarithm is truly an exponent and as such follows the same rules of multiplication and division as other exponents. In multiplication and division we have

$$\log (n \times m) = \log n + \log m$$

$$\log \left(\frac{n}{m}\right) = \log n - \log m$$

Furthermore,

$$\log n^m = m \log n$$

so the logarithm of $3^5 = 243$ is

$$\log 3^5 = 5 \log 3 = 5 \times 0.47712 = 2.3856$$

There is no such thing as the logarithm of a negative number, because there is no power to which 10 (or any other base) can be raised to give a negative number.

A frequently used base for logarithms is the number e ($e = 2.7182818. \ . \ . $). The logarithm to the base e is called the **natural logarithm** and is indicated by $\log_e$ or ln. Base-e logarithms are related to base-10 logarithms by the formula

$$\ln n = 2.3025851 \log n$$

As already stated, calculations of logarithms and powers are inverse operations. Thus, if we want to find the number for which 3.8639 is the common logarithm, we simply calculate

$$10^{3.8639} = 7.310 \times 10^3$$

If we need the number for which the natural logarithm is 2.108, we calculate

$$e^{2.108} = 8.23$$

As before, the number of significant digits in the answer should correspond to the number of digits in the *mantissa* of the logarithm.

C.4 Slopes of Curves and Derivatives

Very frequently in science, one measured quantity depends on a second one. If the property y depends on a second property x, we can write $y = f(x)$, where f is a function that expresses the dependence of y on x. Often, we are interested in the effect of a small change Δx on the dependent variable y. If x changes to $x + \Delta x$, then y will change to $y + \Delta y$. How is Δy related to Δx? Suppose we have the simple linear relation between y and x

$$y = mx + b$$

where m and b are constants. If we substitute $y + \Delta y$ and $x + \Delta x$, we find

$$y + \Delta y = m(x + \Delta x) + b$$

Subtracting the first equation from the second leaves

$$\Delta y = m\Delta x$$

or

$$\frac{\Delta y}{\Delta x} = m$$

The change in y is proportional to the change in x, with a proportionality constant equal to the slope of the line in the graph of y against x.

Suppose now we have a slightly more complicated relationship such as

$$y = ax^2$$

where a is a constant. If we substitute $y = y + \Delta y$ and $x = x + \Delta x$ here, we find

$$\begin{aligned} y + \Delta y &= a(x + \Delta x)^2 \\ &= ax^2 + ax\,\Delta x + (\Delta x)^2 \end{aligned}$$

Subtracting as before leaves

$$\Delta y = 2ax\,\Delta x + (\Delta x)^2$$

Here we have a more complicated, nonlinear relationship between Δy and Δx. If Δx is small enough, however, the term $(\Delta x)^2$ will be small relative to the term proportional to Δx, and we may write

$$\Delta y \approx 2ax\,\Delta x \qquad (\Delta x \text{ small})$$

$$\frac{\Delta y}{\Delta x} \approx 2ax \qquad (\Delta x \text{ small})$$

How do we indicate this graphically? The graph of y against x is no longer a straight line, so we need to generalize the concept of slope. We define a **tangent line** at the point x_0 as the line that touches the graph of $f(x)$ at $x = x_0$ without crossing it.[1] If Δy and Δx are small (Fig. C.2), the slope of the tangent line is

$$\frac{\Delta y}{\Delta x} = 2ax_0 \quad \text{at} \quad x = x_0$$

for the example just discussed. Clearly, the slope is not constant but changes with x_0. If we define the slope at each point on the curve by the slope of the corresponding tangent line, we obtain a *new* function that gives the slope of the curve $f(x)$ at each point x. We call this new function the **derivative** of $f(x)$ and represent it with df/dx. We have already calculated the derivatives of two functions:

$$f(x) = mx + b \Rightarrow \frac{df}{dx} = m$$

$$f(x) = ax^2 \Rightarrow \frac{df}{dx} = ax$$

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[1] This is an intuitive, rather than a rigorously mathematical, definition of a tangent line.

FIGURE C.2 The slope of a curve at a point.

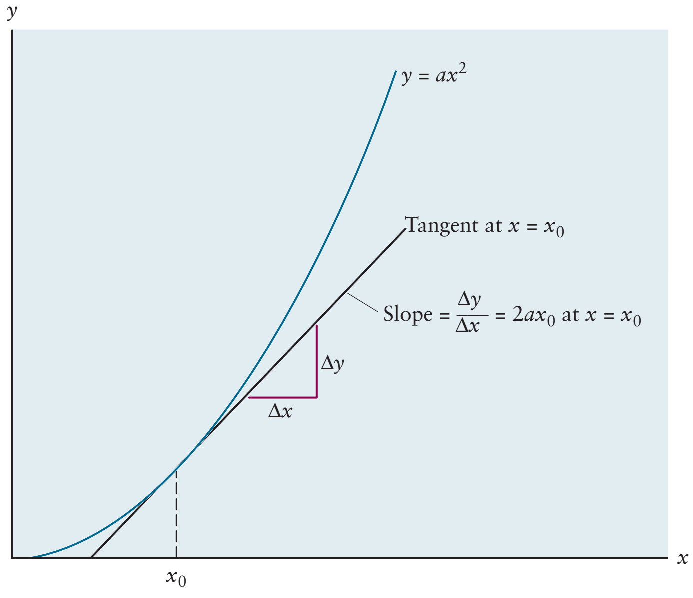

TABLE C.1 Derivatives of Simple Functions

Function $f(x)$	Derivative $\frac{df}{dx}$
$mx + b$	m
ax^2	$2ax$
$\frac{a}{x} = ax^{-1}$	$-\frac{a}{x^2} = -ax^{-2}$
ax^n	nax^{n-1}
e^{ax}	ae^{ax}
$\ln ax$	$\frac{1}{x}$
$\sin ax$	$a \cos ax$
$\cos ax$	$-a \sin ax$

The constants a, b, m, and n may be positive or negative.

Table C.1 shows derivatives of several other functions that are important in basic chemistry.

The derivative gives the slope of the tangent line to $f(x)$ at each point x and can be used to approximate the response to a small perturbation Δx in the independent variable x:

$$\Delta y \approx \frac{df}{dx} \Delta x$$

As an example, consider 1.00 mol of an ideal gas at 0°C that obeys the law

$$P\text{ (atm)} = \frac{22.414 \text{ L atm}}{V(\text{L})}$$

Suppose V is 20.00 L. If the volume V is changed by a small amount ΔV at fixed T and number of moles, what will be the corresponding change ΔP in the pressure? We write

$$P = f(V) = \frac{22.414}{V} = \frac{a}{V}$$

$$\frac{dP}{dV} = \frac{df}{dV} = -\frac{a}{V^2} = -\frac{22.414}{V^2} \qquad \text{(from Table C.1)}$$

$$\Delta P \approx \frac{dP}{dV} \Delta V = -\frac{22.414}{V^2} (\Delta V)$$

If $V = 20.00$ L, then

$$\Delta P \approx -\frac{22.414 \text{ L atm}}{(200.00 \text{ L})^2} \Delta V = -(0.0560 \text{ atm L}^{-1})\, \Delta V$$

C.5 Areas under Curves and Integrals

Another mathematical operation that arises frequently in science is the calculation of the area under a curve. Some areas are those of simple geometric shapes and are easy to calculate. If the function $f(x)$ is a constant,

$$f(x) = a$$

then the area under a graph of $f(x)$ between the two points x_1 and x_2 is that of a rectangle (Fig. C.3a) and is easily calculated as

$$\text{area} = \text{height} \times \text{base} = a(x_2 - x_1) = [ax_2] - [ax_1]$$

If $f(x)$ is a straight line that is neither horizontal nor vertical,

$$f(x) = mx + b$$

then the area is that of a trapezoid (Fig. C.3b) and is equal to

$$\begin{aligned} \text{area} &= \text{average height} \times \text{base} \\ &= \tfrac{1}{2}(mx_1 + b + mx_2 + b)(x_2 - x_1) \\ &= [\tfrac{1}{2} mx_2^2 + bx_2] - [\tfrac{1}{2} mx_1^2 + bx_1] \end{aligned}$$

Suppose now that $f(x)$ is a more complicated function, such as that shown in Figure C.3c. We can estimate the area under this graph by approximating it with a series of small rectangles of width Δx and varying heights. If the height of the ith rectangle is $y_i = f(x_i)$, then we have, approximately,

$$\begin{aligned} \text{area} &\approx f(x_1)\, \Delta x + f(x_2)\, \Delta x + \ldots \\ &= \sum_i f(x_i)\, \Delta x \end{aligned}$$

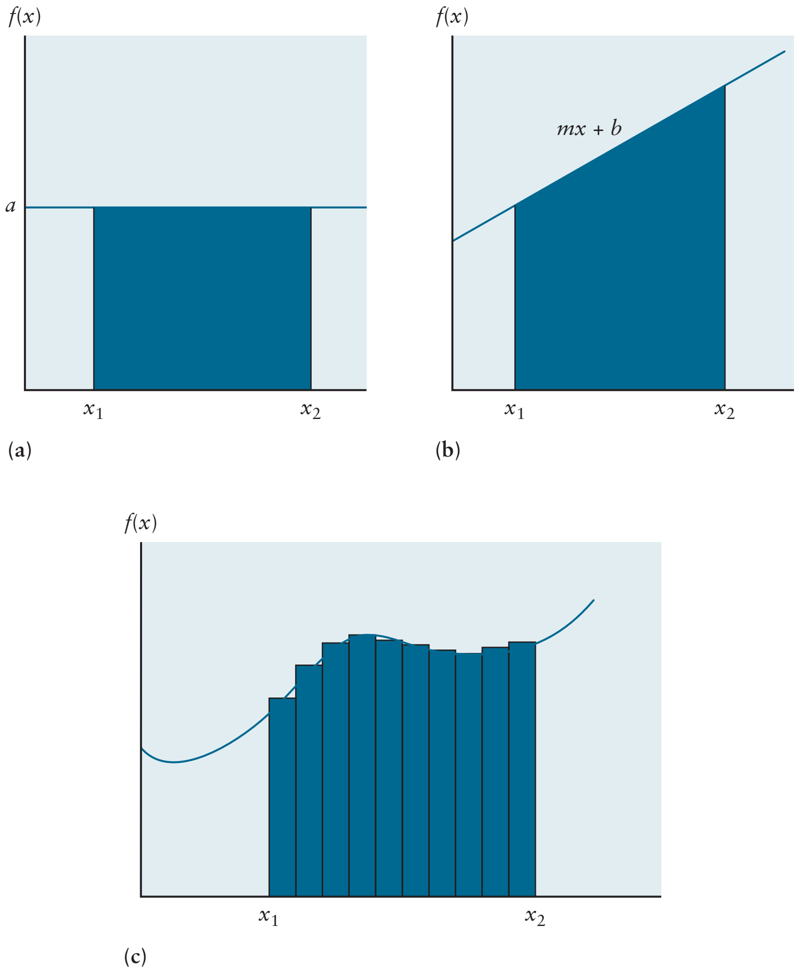

FIGURE C.3 The integral as the area under a curve.

As the widths of the rectangles Δx become small, this becomes a better approximation. We *define* the area under a curve $f(x)$ between two points as the limiting value of this sum as Δx approaches 0, called the **definite integral:**

$$\text{area} = \int_{x_1}^{x_2} f(x)\,dx$$

We have already worked out two examples of such integrals:

$$f(x) = a \Rightarrow \int_{x_1}^{x_2} a\,dx = [ax_2] - [ax_1]$$

$$f(x) = ax + b \Rightarrow \int_{x_1}^{x_2} (ax + b)\,dx = [\tfrac{1}{2}ax_2^2 + bx_2] - [\tfrac{1}{2}ax_1^2 + bx_1]$$

These integrals have an interesting form, which can be generalized to other cases as well: some function F evaluated at the upper limit (x_2) minus that function F evaluated at the lower limit (x_1).

$$\int_{x_1}^{x_2} f(x)\,dx = F(x_2) - F(x_1)$$

F is called the **antiderivative** of f because, for reasons we shall not go into here, it is obtained by the inverse of a derivative operation. In other words, if F is the antiderivative of f, then f is the derivative of F:

$$\frac{dF}{dx} = f(x)$$

TABLE C.2 Integrals of Simple Functions

Function $f(x)$	Antiderivative $F(x)$	Integral $\int_{x_1}^{x_2} f(x)\,dx$
a	ax	$ax_2 - ax_1$
$mx + b$	$\frac{1}{2}mx^2 + bx$	$[\frac{1}{2}mx_2^2 + bx_2] - [\frac{1}{2}mx_1^2 - bx_1]$
x^n $(n \neq -1)$	$\frac{1}{n+1}x^{n+1}$	$\frac{1}{n+1}(x_1^{n+1} - x_1^{n+1})$
$\frac{1}{x} = x^{-1}$ $(x > 0)$	$\ln x$	$(\ln x_2 - \ln x_1) = \ln \frac{x_2}{x_1}$
$\frac{1}{x^2} = x^{-2}$	$-\frac{1}{x}$	$-\left(\frac{1}{x_2} - \frac{1}{x_1}\right)$
e^{ax}	$\frac{e^{ax}}{a}$	$\frac{1}{a}(e^{ax_2} - e^{ax_1})$

The constants a, b, m, and n may be positive or negative.

To calculate integrals, therefore, we invert the results of Table C.1, because we need to find those functions $F(x)$ whose derivatives are equal to $f(x)$. Table C.2 lists several of the most important integrals for basic chemistry.

Several additional mathematical properties of integrals are important at this point. If a function is multiplied by a constant c, then the integral is multiplied by the same constant:

$$\int_{x_1}^{x_2} cf(x)\,dx = c\int_{x_1}^{x_2} f(x)\,dx$$

The reason is self-evident: if a function is multiplied everywhere by a constant factor, then the area under its graph must be increased by the same factor. Second, the integral of the sum of two functions is the sum of the separate integrals:

$$\int_{x_1}^{x_2} [f(x) + g(x)]\,dx = \int_{x_1}^{x_2} f(x)\,dx + \int_{x_1}^{x_2} g(x)\,dx$$

Finally, if the upper and lower limits of integration are reversed, the sign of the integral changes as well. This is easily seen from the antiderivative form:

$$\int_{x_2}^{x_1} f(x)\,dx = F(x_1) - F(x_2) = -[F(x_2) - F(x_1)] = -\int_{x_1}^{x_2} f(x)\,dx$$

C.6 Probability

Many applications in chemistry require us to interpret—and even predict—the results of measurements where we have only limited information about the system and the process involved. In such cases the best we can do is identify the possible outcomes of the experiment and assign a *probability* to each of them. Two examples illustrate the issues we face. In discussions of atomic structure, we would like to know the position of an electron relative to the nucleus. The principles of quantum mechanics tell us we can never know the exact location or trajectory of an electron; the most information we can have is the probability of finding an electron at each point in space around the nucleus. In discussing the behavior of a macroscopic amount of helium gas confined at a particular volume, pressure, and temperature we would like to know the speed with which an atom is moving in the container. We do not have experimental means to "tag" a particular atom, track its motions in the container, and measure its speed. The best we can do is estimate the probability that some typical atom is moving with each possible speed.

Everyone is familiar with the common sense concept of probability as a way to assess the likelihood of a desirable outcome in a game of chance. The purpose of this section is to give a brief introduction to probability in a form suited for scientific work.

Random Variable

The first step in setting up a probability model of a statistical experiment is to define the **random variable *X*,** the measurable quantity whose values *fluctuate,* or change, as we carry out many repetitions of the experiment. While defining the random variable, we also identify the **outcomes** of the statistical experiment, the possible values that X can take as we carry out many repetitions. If the experiment consists of flipping a coin, then X is simply the label on the side of the coin facing up, and the only possible outcomes are H for "heads" and T for "tails." If the experiment consists of rolling a die, X is the number of dots on the side facing up, with integral values from 1 to 6. If the experiment is rolling a pair of dice, X is the sum of the number of dots on the two sides facing up, with integral values from $1 + 1 = 2$ to $6 + 6 = 12$. If the experiment is to find the position of an electron in an atom, X is then r, the distance from the nucleus to the electron, and it can range from 0 to infinity. If the experiment is to find the speed of an atom in a sample of gas, X is then u, the speed of the atom, which can range from 0 to some large value.

Probability and Probability Functions

It is convenient to set up a graphical representation of the probability model. We represent the random variable X along the horizontal axis of an ordinary Cartesian graph. The possible outcomes of measuring X are shown as points along the horizontal axis. We see from the earlier examples that these can be either discrete or continuous values, depending on the nature of X. Along the vertical axis we want to plot $P(X)$, the probability of observing the random variable to have the value X, for each of the possible outcomes.

The **probability function *P*(*X*)** is generated by making multiple measurements of the random variable X and recording the results in a histogram. The performance of a chemistry class with 50 students on a quiz with maximum score 20 is a good example of a statistical experiment. Here the random variable X is the score a student achieves, and the possible outcomes are the integers from 0 to 20. The set of graded papers constitute 50 repetitions of the statistical experiment, and the results are summarized in Figure C.4. We define the probability that a particular score was achieved on the exam to be the fraction of the papers with that score:

$$P(X_i) = \frac{n_i(X_i)}{N}$$

where $n_i(X_i)$ is the number of papers with score X_i and N is the total number of papers. Figure C.5 shows the probability function generated from the data in Figure C.4. The function has a maximum at $X = 14$, which is labeled the **most probable value X_{mp}.** This is the value that appears most often in the experimental data. Probability is a pure number; it does not have physical dimensions. Probability cannot be determined from a single measurement; many repetitions of the statistical experiment are required for the definition of probability.

The probability function has the interesting property that its sum over all the possible outcomes is 1:

$$P_0 + P_1 + \ldots + P_{19} + P_{20} = \frac{1}{50}(n_0 + n_1 + \ldots + n_{19} + n_{20}) = \frac{50}{50} = 1$$

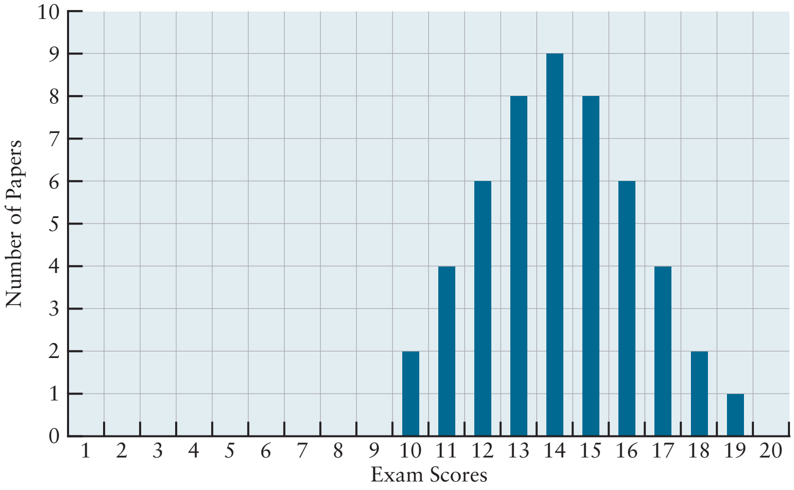

FIGURE C.4 Distribution of exam scores in a class of 50 students.

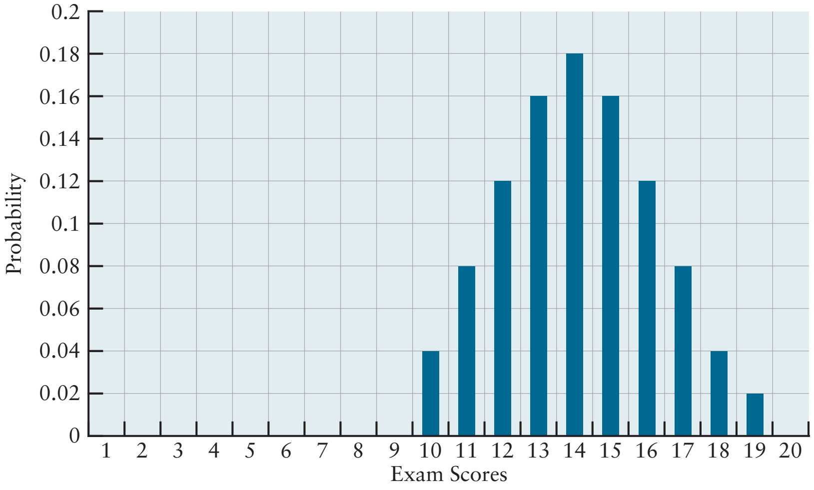

FIGURE C.5 Probability function for the exam scores in Figure C.4.

We represent this long sum in the following compact way where the uppercase Greek sigma means "add up all the terms," and the running index *i* indicates the term for each possible outcome from 0 to 20:

$$\sum_{i=0}^{20} P_i = \frac{1}{50}\sum_{i=0}^{20} n_i = \frac{50}{50} = 1$$

A probability function with this property is said to be **normalized.** Normalization signifies that we have accounted for all the possible outcomes: the probability that *some* score is achieved is 1. We should always check that a probability function is normalized before using it in further calculations.

Average Values of the Random Variable

The probability function is used in numerous statistical analyses of the experiment, only one of which we describe here. We calculate $\overline{X}$, the *mean,* or average, value of the random variable, by multiplying each possible outcome by its probability and summing over all the possible outcomes. In our compact form this operation for the probability function in Figure C.5 is

$$\overline{X} = \sum_{i=0}^{20} X_i P(X_i) = \frac{1}{50}\sum_{i=0}^{20} X_i n_i = 14.7$$

The mean value is one way to convey the essence of the probability function in a single number: Is the overall class performance on the exam good, fair, or poor? Another way is to state the most probable value X_{mp}. In this example the mean value is slightly larger than the most probable value because the distribution slightly favors the high end of the range, courtesy of the student who scored 19 of 20! The mean and most probable values coincide only when the distribution is perfectly symmetrical about the maximum. The complete probability function gives much more insight into the results of the experiment than the mean or most probable values standing alone.

Probability Density: Continuous Random Variables and Probability Functions

When the random variable is continuous, as in the case of the position of the electron and speed of the helium atom referred to earlier, we must consider every point of the X axis—not just the integers—as a possible outcome. Therefore, we cannot define the probability of observing a specific value, which we call X_0. Rather, we define the probability that X falls within a narrow, infinitesimal interval between X_0 and $X_0 + \mathrm{d}X$. When the interval $\mathrm{d}X$ is sufficiently small, the probability will be proportional to the width of the interval, and we define the probability as follows:

$$[\text{Probability of } X \text{ falling in the interval between } X_0 \text{ and } X_0 + \mathrm{d}X] = \mathcal{P}(X_0)\mathrm{d}X$$

Because this analysis is required at each point X, we drop the subscript 0, and discuss the properties of $\mathcal{P}(X)$ in general. The function $\mathcal{P}(X)$, called the **probability density function** for X, is plotted as a continuous function above the X-axis. It is defined for all points in an interval (a, b) whose end points depend on the nature of X. In some cases the end points can include $+\infty, -\infty$, or both. Note that $\mathcal{P}(X)$ has physical dimensions of X^{-1}, since the product $\mathcal{P}(X)\mathrm{d}X$ must be dimensionless.

The probability density plays the same role for continuous variables as does $P(X)$ for discrete random variables. The normalization condition becomes

$$\int_a^b \mathcal{P}(X)\mathrm{d}X = 1$$

and the mean value of X is calculated as

$$\overline{X} = \int_a^b X \cdot \mathcal{P}(X)\mathrm{d}X$$

The symmetry of the probability density function determines whether the most probable and mean values of X coincide. We use a special symbol here to distinguish probability density from probability. In the main portion of the textbook we do not always make that distinction in symbols. But, it is always clear from context whether we are discussing a probability function or a probability density function.

Experimental Tests of Theoretical Probability

Theoretical probability identifies the possible outcomes of a statistical experiment, and uses theoretical arguments to predict the probability of each. Many applications in chemistry take this form. In atomic and molecular structure problems, the general principles of quantum mechanics predict the probability functions. In other cases the theoretical predictions are based on assumptions about the chemical or physical behavior of a system. In all cases, the validity of these predictions must be tested by comparison with laboratory measurements of the behavior of the same random variable. A full determination of experimental probability, and the mean values that come from it, must be obtained and compared with the theoretical predictions. A theoretical prediction of probability can never be tested or interpreted with a single measurement. A large number of repeated measurements is necessary to reveal the true statistical behavior.

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G.

Using Graphs

1. A particular plot of distance traveled against time elapsed is found to be a straight line. After an elapsed time of 1.5 hours, the distance traveled was 75 miles, and after an elapsed time of 3.0 hours, the distance traveled was 150 miles. Calculate the slope of the plot of distance against time, and give its units.

2. The pressure of a gas in a rigid container is measured at several different temperatures, and it is found that a plot of pressure against temperature is a straight line. At 20.0°C the pressure is 4.30 atm, and at 100.0°C the pressure is 5.47 atm. Calculate the slope of the plot of pressure against temperature and give its units.

3. Rewrite each of the following linear equations in the form $y = mx + b$, and give the slope and intercept of the corresponding plot. Then draw the graph.
(a) $y = 4x - 7$
(b) $7x - 2y = 5$
(c) $3y + 6x - 4 = 0$

4. Rewrite each of the following linear equations in the form $y = mx + b$, and give the slope and intercept of the corresponding plot. Then draw the graph.
(a) $y = -2x - 8$
(b) $-3x + 4y = 7$
(c) $7y - 16x + 53 = 0$

5. Graph the relation

$$y = 2x^3 - 3x^2 + 6x - 5$$

from $y = -2$ to $y = +2$. Is the plotted curve a straight line?

6. Graph the relation

$$y = \frac{8 - 10x - 3x^2}{2 - 3x}$$

from $x = -3$ to $x = +3$. Is the plotted curve a straight line?

Solution of Algebraic Equations

7. Solve the following linear equations for x.
(a) $7x + 5 = 0$
(b) $-4x + 3 = 0$
(c) $-3x = -2$

8. Solve the following linear equations for x.
(a) $6 - 8x = 0$
(b) $-2x - 5 = 0$
(c) $4x = -8$

9. Solve the following quadratic equations for x.
(a) $4x^2 + 7x - 5 = 0$
(b) $2x^2 = -3 - 6x$
(c) $2x + \dfrac{3}{x} = 6$

10. Solve the following quadratic equations for x.
(a) $6x^2 + 15x + 2 = 0$
(b) $4x = 5x^2 - 3$
(c) $\dfrac{1}{2 - x} + 3x = 4$

11. Solve each of the following equations for x using the approximation of small x, iteration, or graphical solution, as appropriate.
(a) $x(2.00 + x)^2 = 2.6 \times 10^{-6}$
(b) $x(3.00 - 7x)(2.00 + 2x) = 0.230$
(c) $2x^3 + 3x^2 + 12x = -16$

12. Solve each of the following equations for x using the approximation of small x, iteration, or graphical solution, as appropriate.
(a) $x(2.00 + x)(3.00 - x)(5.00 + 2x) = 1.58 \times 10^{-15}$
(b) $x\dfrac{(3.00 + x)(1.00 - x)}{2.00 - x} = 0.122$
(c) $12x^3 - 4x^2 + 35x = 10$

Powers and Logarithms

13. Calculate each of the following expressions, giving your answers the proper numbers of significant figures.
(a) $\log(3.56 \times 10^4)$
(b) $e^{-15.69}$
(c) $10^{8.41}$
(d) $1\text{n}(6.893 \times 10^{-22})$

14. Calculate each of the following expressions, giving your answers the proper numbers of significant figures.
(a) $10^{-16.528}$
(b) $\ln(4.30 \times 10^{13})$
(c) $e^{14.21}$
(d) $\log(4.983 \times 10^{-11})$

15. What number has a common logarithm of 0.4793?

16. What number has a natural logarithm of −15.824?

17. Determine the common logarithm of 3.00×10^{121}. It is quite likely that your calculator will *not* give a correct answer. Explain why.

18. Compute the value of $10^{-107.8}$. It is quite likely that your calculator will *not* give the correct answer. Explain why.

19. The common logarithm of 5.64 is 0.751. Without using a calculator, determine the common logarithm of 5.64×10^7 and of 5.64×10^{-3}.

20. The common logarithm of 2.68 is 0.428. Without using a calculator, determine the common logarithm of 2.68×10^{192} and of 2.68×10^{-289}.

21. Use the graphical method and a calculator to solve the equation

$$\log \ln x = -x$$

for x. Give x to four significant figures.

22. Use a calculator to find a number that is equal to the reciprocal of its own natural logarithm. Report the answer to four significant figures.

Slopes of Curves and Derivatives

23. Calculate the derivatives of the following functions.
 (a) $y = 4x^2 + 4$
 (b) $y = \sin 3x + 4 \cos 2x$
 (c) $y = 3x + 2$
 (d) $y = \ln 7x$

24. Calculate the derivatives of the following functions.
 (a) $y = 6x^{19}$
 (b) $y = 7x^2 + 6x + 2$
 (c) $y = e^{-6x}$
 (d) $y = \cos 2x + \dfrac{7}{x}$

Areas under Curves and Integrals

25. Calculate the following integrals.
 (a) $\displaystyle\int_2^4 (3x + 1)dx$
 (b) $\displaystyle\int_0^5 x^6\, dx$
 (c) $\displaystyle\int_1^4 e^{-2x}\, dx$

26. Calculate the following integrals.
 (a) $\displaystyle\int_{-1}^3 4\, dx$
 (b) $\displaystyle\int_2^{100} \frac{1}{x}\, dx$
 (c) $\displaystyle\int_2^4 \frac{5}{x^2}\, dx$

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APPENDIX D

Standard Chemical Thermodynamic Properties

This table lists standard enthalpies of formation ΔH_f°, standard third-law entropies S°, standard free energies of formation ΔG_f°, and molar heat capacities at constant pressure, C_P, for a variety of substances, all at 25°C (298.15 K) and 1 atm. The table proceeds from the left side to the right side of the periodic table. Binary compounds are listed under the element that occurs to the left in the periodic table, except that binary oxides and hydrides are listed with the other element. Thus, KCl is listed with potassium and its compounds, but ClO_2 is listed with chlorine and its compounds.

Note that the *solution-phase* entropies are not absolute entropies but are measured relative to the arbitrary standard $S^\circ(H^+(aq)) = 0$. Consequently, some of them (as well as some of the heat capacities) are negative.

Most of the thermodynamic data in these tables were taken from the *NBS Tables of Chemical Thermodynamic Properties* (1982) and changed, where necessary, from a standard pressure of 0.1 MPa to 1 atm. The data for organic compounds $C_nH_m (n > 2)$ were taken from the *Handbook of Chemistry and Physics* (1981).

Substance	ΔH_f° (25°C) kJ mol^{-1}	S° (25°C) J K^{-1} mol^{-1}	ΔG_f° (25°C) kJ mol^{-1}	C_P (25°C) J K^{-1} mol^{-1}
$H(g)$	217.96	114.60	203.26	20.78
$H_2(g)$	0	130.57	0	28.82
$H^+(aq)$	0	0	0	0
$H_3O^+(aq)$	−285.83	69.91	−237.18	75.29
$Li(s)$	0	29.12	0	24.77
$Li(g)$	159.37	138.66	126.69	20.79
$Li^+(aq)$	−278.49	13.4	−293.31	68.6
$LiH(s)$	−90.54	20.01	−68.37	27.87
$Li_2O(s)$	−597.94	37.57	−561.20	54.10
$LiF(s)$	−615.97	35.65	−587.73	41.59
$LiCl(s)$	−408.61	59.33	−384.39	47.99
$LiBr(s)$	−351.21	74.27	−342.00	—
$LiI(s)$	−270.41	86.78	−270.29	51.04
$Na(s)$	0	51.21	0	28.24
$Na(g)$	107.32	153.60	76.79	20.79
$Na^+(aq)$	−240.12	59.0	−261.90	46.4
$Na_2O(s)$	−414.22	75.06	−375.48	69.12
$NaOH(s)$	−425.61	64.46	−379.53	59.54
$NaF(s)$	−573.65	51.46	−543.51	48.86
$NaCl(s)$	−411.15	72.13	−384.15	50.50

continued

	Substance	ΔH_f° (25°C) kJ mol^{-1}	S° (25°C) J K^{-1} mol^{-1}	ΔG_f° (25°C) kJ mol^{-1}	C_P (25°C) J K^{-1} mol^{-1}
	$NaBr(s)$	−361.06	86.82	−348.98	51.38
	$NaI(s)$	−287.78	98.53	−286.06	52.09
	$NaNO_3(s)$	−467.85	116.52	−367.07	92.88
	$Na_2S(s)$	−364.8	83.7	−349.8	—
	$Na_2SO_4(s)$	−1387.08	149.58	−1270.23	128.20
	$NaHSO_4(s)$	−1125.5	113.0	−992.9	—
	$Na_2CO_3(s)$	−1130.68	134.98	−1044.49	112.30
	$NaHCO_3(s)$	−950.81	101.7	−851.1	87.61
	$K(s)$	0	64.18	0	29.58
	$K(g)$	89.24	160.23	60.62	20.79
	$K^+(aq)$	−252.38	102.5	−283.27	21.8
	$KO_2(s)$	−284.93	116.7	−239.4	77.53
	$K_2O_2(s)$	−494.1	102.1	−425.1	—
	$KOH(s)$	−424.76	78.9	−379.11	64.9
	$KF(s)$	−567.27	66.57	−537.77	49.04
	$KCl(s)$	−436.75	82.59	−409.16	51.30
	$KClO_3(s)$	−397.73	143.1	−296.25	100.25
	$KBr(s)$	−393.80	95.90	−380.66	52.30
	$KI(s)$	−327.90	106.32	−324.89	52.93
	$KMnO_4(s)$	−837.2	171.71	−737.7	117.57
	$K_2CrO_4(s)$	−1403.7	200.12	−1295.8	145.98
	$K_2Cr_2O_7(s)$	−2061.5	291.2	−1881.9	219.24
	$Rb(s)$	0	76.78	0	31.06
	$Rb(g)$	80.88	169.98	53.09	20.79
	$Rb^+(aq)$	−251.17	121.50	−283.98	—
	$RbCl(s)$	−435.35	95.90	−407.82	52.38
	$RbBr(s)$	−394.59	109.96	−381.79	52.84
	$RbI(s)$	−333.80	118.41	−328.86	53.18
	$Cs(s)$	0	85.23	0	32.17
	$Cs(g)$	76.06	175.49	49.15	70.79
	$Cs^+(aq)$	−258.28	133.05	−292.02	−10.5
	$CsF(s)$	−553.5	92.80	−525.5	51.09
	$CsCl(s)$	−443.04	101.17	−414.55	52.47
	$CsBr(s)$	−405.81	113.05	−391.41	52.93
	$CsI(s)$	−346.60	123.05	−340.58	52.80
II	$Be(s)$	0	9.50	0	16.44
	$Be(g)$	324.3	136.16	286.6	20.79
	$BeO(s)$	−609.6	14.14	−580.3	25.52
	$Mg(s)$	0	32.68	0	24.89
	$Mg(g)$	147.70	148.54	113.13	20.79
	$Mg^{2+}(aq)$	−466.85	−138.1	−454.8	—
	$MgO(s)$	−601.70	26.94	−569.45	37.15
	$MgCl_2(s)$	−641.32	89.62	−591.82	71.38
	$MgSO_4(s)$	−1284.9	91.6	−1170.7	96.48
	$Ca(s)$	0	41.42	0	25.31
	$Ca(g)$	178.2	154.77	144.33	20.79
	$Ca^{2+}(aq)$	−542.83	−53.1	−553.58	—
	$CaH_2(s)$	−186.2	42	−147.2	—
	$CaO(s)$	−635.09	39.75	−604.05	42.80
	$CaS(s)$	−482.4	56.5	−477.4	47.40
	$Ca(OH)_2(s)$	−986.09	83.39	−898.56	87.49
	$CaF_2(s)$	−1219.6	68.87	−1167.3	67.03
	$CaCl_2(s)$	−795.8	104.6	−748.1	72.59
	$CaBr_2(s)$	−682.8	130	−663.6	—
	$CaI_2(s)$	−533.5	142	−528.9	—
	$Ca(NO_3)_2(s)$	−938.39	193.3	−743.20	149.37
	$CaC_2(s)$	−59.8	69.96	−64.9	62.72

continued

Substance	**ΔH_f° (25°C) kJ mol^{-1}**	**S° (25°C) J K^{-1} mol^{-1}**	**ΔG_f° (25°C) kJ mol^{-1}**	**C_P (25°C) J K^{-1} mol^{-1}**
$CaCO_3$(*s*, calcite)	−1206.92	92.9	−1128.84	81.88
$CaCO_3$(*s*, aragonite)	−1207.13	88.7	−1127.80	81.25
$CaSO_4$(*s*)	−1434.11	106.9	−1321.86	99.66
$CaSiO_3$(*s*)	−1634.94	81.92	−1549.66	85.27
$CaMg(CO_3)_2$ (*s*, dolomite)	−2326.3	155.18	−2163.4	157.53
Sr(*s*)	0	52.3	0	26.4
Sr(*g*)	164.4	164.51	130.9	20.79
Sr^{2+}(*aq*)	−545.80	−32.6	−559.48	—
$SrCl_2$(*s*)	−828.9	114.85	−781.1	75.60
$SrCO_3$(*s*)	−1220.0	97.1	−1140.1	81.42
Ba(*s*)	0	62.8	0	28.07
Ba(*g*)	180	170.24	146	20.79
Ba^{2+}(*aq*)	−537.64	9.6	−560.77	—
$BaCl_2$(*s*)	−858.6	123.68	−810.4	75.14
$BaCO_3$(*s*)	−1216.3	112.1	−1137.6	85.35
$BaSO_4$(*s*)	−1473.2	132.2	−1362.3	101.75
Sc(*s*)	0	34.64	0	25.52
Sc(*g*)	377.8	174.68	336.06	22.09
Sc^{3+}(*aq*)	−614.2	−255	−586.6	—
Ti(*s*)	0	30.63	0	25.02
Ti(*g*)	469.9	180.19	425.1	24.43
TiO_2(*s*, rutile)	−944.7	50.33	−889.5	55.02
$TiCl_4$(ℓ)	−804.2	252.3	−737.2	145.18
$TiCl_4$(*g*)	−763.2	354.8	−726.8	95.4
Cr(*s*)	0	23.77	0	23.35
Cr(*g*)	396.6	174.39	351.8	20.79
Cr_2O_3(*s*)	−1139.7	81.2	−1058.1	118.74
CrO_4^{2-}(*aq*)	−881.15	50.21	−727.75	—
$Cr_2O_7^{2-}$(*aq*)	−1490.3	261.9	−1301.1	—
W(*s*)	0	32.64	0	24.27
W(*g*)	849.4	173.84	807.1	21.31
WO_2(*s*)	−589.69	50.54	−533.92	56.11
WO_3(*s*)	−842.87	75.90	−764.08	73.76
Mn(*s*)	0	32.01	0	26.32
Mn(*g*)	280.7	238.5	173.59	20.79
Mn^{2+}(*aq*)	−220.75	−73.6	−228.1	50
MnO(*s*)	−385.22	59.71	−362.92	45.44
MnO_2(*s*)	−520.03	53.05	−465.17	54.14
MnO_4^-(*s*)	−541.4	191.2	−447.2	−82.0
Fe(*s*)	0	27.28	0	25.10
Fe(*g*)	416.3	180.38	370.7	25.68
Fe^{2+}(*aq*)	−89.1	−137.7	−78.9	—
Fe^{3+}(*aq*)	−48.5	−315.9	−4.7	—
$Fe_{0.947}O$(*s*, wüstite)	−266.27	57.49	−245.12	48.12
Fe_2O_3(*s*, hematite)	−824.2	87.40	−742.2	103.85
Fe_3O_4(*s*, magnetite)	−1118.4	146.4	−1015.5	143.43
$Fe(OH)_3$(*s*)	−823.0	106.7	−696.5	—
FeS(*s*)	−100.0	60.29	−100.4	50.54
$FeCO_3$(*s*)	−740.57	93.1	−666.72	82.13
$Fe(CN)_6^{3-}$(*aq*)	561.9	270.3	729.4	—
$Fe(CN)_6^{4-}$(*aq*)	455.6	95.0	695.1	—

continued

	Substance	ΔH_f° (25°C) kJ mol^{-1}	S° (25°C) J K^{-1} mol^{-1}	ΔG_f° (25°C) kJ mol^{-1}	C_P (25°C) J K^{-1} mol^{-1}
	$Co(s)$	0	30.04	0	24.81
	$Co(g)$	424.7	179.41	380.3	23.02
	$Co^{2+}(aq)$	−58.2	−113	−54.4	—
	$Co^{3+}(aq)$	92	−305	134	—
	$CoO(s)$	−237.94	52.97	−214.22	55.23
	$CoCl_2(s)$	−312.5	109.16	−269.8	78.49
	$Ni(s)$	0	29.87	0	26.07
	$Ni(g)$	429.7	182.08	384.5	25.36
	$Ni^{2+}(aq)$	−54.0	−128.9	−45.6	—
	$NiO(s)$	−239.7	37.99	−211.7	44.31
	$Pt(s)$	0	41.63	0	25.86
	$Pt(g)$	565.3	192.30	520.5	25.53
	$PtCl_6^{2-}(aq)$	−668.2	219.7	−482.7	—
	$Cu(s)$	0	33.15	0	24.44
	$Cu(g)$	338.32	166.27	298.61	20.79
	$Cu^{+}(aq)$	71.67	40.6	49.98	—
	$Cu^{2+}(aq)$	64.77	−99.6	65.49	—
	$CuO(s)$	−157.3	42.63	−129.7	42.30
	$Cu_2O(s)$	−168.6	93.14	−146.0	63.64
	$CuCl(s)$	−137.2	86.2	−119.88	48.5
	$CuCl_2(s)$	−220.1	108.07	−175.7	71.88
	$CuSO_4(s)$	−771.36	109	−661.9	100.0
	$Cu(NH_3)_4^{2+}(aq)$	−348.5	273.6	−111.07	—
	$Ag(s)$	0	42.55	0	25.35
	$Ag(g)$	284.55	172.89	245.68	20.79
	$Ag^{+}(aq)$	105.58	72.68	77.11	21.8
	$AgCl(s)$	−127.07	96.2	−109.81	50.79
	$AgNO_3(s)$	−124.39	140.92	−33.48	93.05
	$Ag(NH_3)_2^{+}(aq)$	−111.29	245.2	−17.12	—
	$Au(s)$	0	47.40	0	25.42
	$Au(g)$	366.1	180.39	326.3	20.79
	$Zn(s)$	0	41.63	0	25.40
	$Zn(g)$	130.73	160.87	95.18	20.79
	$Zn^{2+}(aq)$	−153.89	−112.1	−147.06	46
	$ZnO(s)$	−348.28	43.64	−318.32	40.25
	ZnS(*s*, sphalerite)	−205.98	57.7	−201.29	46.0
	$ZnCl_2(s)$	−415.05	111.46	−369.43	71.34
	$ZnSO_4(s)$	−982.8	110.5	−871.5	99.2
	$Zn(NH_3)_4^{2+}(aq)$	−533.5	301	−301.9	—
	$Hg(\ell)$	0	76.02	0	27.98
	$Hg(g)$	61.32	174.85	31.85	20.79
	$HgO(s)$	−90.83	70.29	−58.56	44.06
	$HgCl_2(s)$	−224.3	146.0	−178.6	—
	$Hg_2Cl_2(s)$	−265.22	192.5	−210.78	—
III	$B(s)$	0	5.86	0	11.09
	$B(g)$	562.7	153.34	518.8	20.80
	$B_2H_6(g)$	35.6	232.00	86.6	56.90
	$B_5H_9(g)$	73.2	275.81	174.9	96.78
	$B_2O_3(s)$	−1272.77	53.97	−1193.70	62.93
	$H_3BO_3(s)$	−1094.33	88.83	−969.02	81.38
	$BF_3(g)$	−1137.00	254.01	−1120.35	50.46
	$BF_4^{-}(aq)$	−1574.9	180	−1486.9	—
	$BCl_3(g)$	−403.76	289.99	−388.74	62.72
	$BBr_3(g)$	−205.64	324.13	−232.47	67.78
	$Al(s)$	0	28.33	0	24.35

continued

	Substance	ΔH_f° (25°C) kJ mol^{-1}	S° (25°C) J K^{-1} mol^{-1}	ΔG_f° (25°C) kJ mol^{-1}	C_P (25°C) J K^{-1} mol^{-1}
	$\mathrm{Al}(g)$	326.4	164.43	285.7	21.38
	$\mathrm{Al}^{3+}(aq)$	−531	−321.7	−485	—
	$\mathrm{Al_2O_3}(s)$	−1675.7	50.92	−1582.3	79.04
	$\mathrm{AlCl_3}(s)$	−704.2	110.67	−628.8	91.84
	$\mathrm{Ga}(s)$	0	40.88	0	25.86
	$\mathrm{Ga}(g)$	277.0	168.95	238.9	25.36
	$\mathrm{Tl}(s)$	0	64.18	0	26.32
	$\mathrm{Tl}(g)$	182.21	180.85	147.44	20.79
IV	$\mathrm{C}(s$, graphite$)$	0	5.74	0	8.53
	$\mathrm{C}(s$, diamond$)$	1.895	2.377	2.900	6.11
	$\mathrm{C}(g)$	716.682	157.99	671.29	20.84
	$\mathrm{CH_4}(g)$	−74.81	186.15	−50.75	35.31
	$\mathrm{C_2H_2}(g)$	226.73	200.83	209.20	43.93
	$\mathrm{C_2H_4}(g)$	52.26	219.45	68.12	43.56
	$\mathrm{C_2H_6}(g)$	−84.68	229.49	−32.89	52.63
	$\mathrm{C_3H_8}(g)$	−103.85	269.91	−23.49	73.0
	$n\text{-}\mathrm{C_4H_{10}}(g)$	−124.73	310.03	−15.71	97.5
	$\mathrm{C_4H_{10}}(g$, isobutane$)$	−131.60	294.64	−17.97	96.8
	$n\text{-}\mathrm{C_5H_{12}}(g)$	−146.44	348.40	−8.20	120
	$\mathrm{C_6H_6}(g)$	82.93	269.2	129.66	81.6
	$\mathrm{C_6H_6}(\ell)$	49.03	172.8	124.50	136
	$\mathrm{CO}(g)$	−110.52	197.56	−137.15	29.14
	$\mathrm{CO_2}(g)$	−393.51	213.63	−394.36	37.11
	$\mathrm{CO_2}(aq)$	−413.80	117.6	−385.98	—
	$\mathrm{CS_2}(\ell)$	89.70	151.34	65.27	75.7
	$\mathrm{CS_2}(g)$	117.36	237.73	67.15	45.40
	$\mathrm{H_2CO_3}(aq)$	−699.65	187.4	−623.08	—
	$\mathrm{HCO_3^-}(aq)$	−691.99	91.2	−586.77	—
	$\mathrm{CO_3^{2-}}(aq)$	−677.14	−56.9	−527.81	—
	$\mathrm{HCOOH}(\ell)$	−424.72	128.95	−361.42	99.04
	$\mathrm{HCOOH}(aq)$	−425.43	163	−372.3	—
	$\mathrm{COOH^-}(aq)$	−425.55	92	−351.0	−87.9
	$\mathrm{CH_2O}(g)$	−108.57	218.66	−102.55	35.40
	$\mathrm{CH_3OH}(\ell)$	−238.66	126.8	−166.35	81.6
	$\mathrm{CH_3OH}(g)$	−200.66	239.70	−162.01	43.89
	$\mathrm{CH_3OH}(aq)$	−245.93	133.1	−175.31	—
	$\mathrm{H_2C_2O_4}(s)$	−827.2	—	—	117
	$\mathrm{HC_2O_4^-}(aq)$	−818.4	149.4	−698.34	—
	$\mathrm{C_2O_4^{2-}}(aq)$	−825.1	45.6	−673.9	—
	$\mathrm{CH_3COOH}(\ell)$	−484.5	159.8	−390.0	124.3
	$\mathrm{CH_3COOH}(g)$	−432.25	282.4	−374.1	66.5
	$\mathrm{CH_3COOH}(aq)$	−485.76	178.7	−396.46	—
	$\mathrm{CH_3COO^-}(aq)$	−486.01	86.6	−369.31	−6.3
	$\mathrm{CH_3CHO}(\ell)$	−192.30	160.2	−128.12	—
	$\mathrm{C_2H_5OH}(\ell)$	−277.69	160.7	−174.89	111.46
	$\mathrm{C_2H_5OH}(g)$	−235.10	282.59	−168.57	65.44
	$\mathrm{C_2H_5OH}(aq)$	−288.3	148.5	−181.64	—
	$\mathrm{CH_3OCH_3}(g)$	−184.05	266.27	−112.67	64.39
	$\mathrm{CF_4}(g)$	−925	261.50	−879	61.09
	$\mathrm{CCl_4}(\ell)$	−135.44	216.40	−65.28	131.75
	$\mathrm{CCl_4}(g)$	−102.9	309.74	−60.62	83.30
	$\mathrm{CHCl_3}(g)$	−103.14	295.60	−70.37	65.69
	$\mathrm{COCl_2}(g)$	−218.8	283.53	−204.6	57.66
	$\mathrm{CH_2Cl_2}(g)$	−92.47	270.12	−65.90	50.96
	$\mathrm{CH_3Cl}(g)$	−80.83	234.47	−57.40	40.75
	$\mathrm{CBr_4}(s)$	18.8	212.5	47.7	144.3
	$\mathrm{CH_3I}(\ell)$	−15.5	163.2	13.4	126

continued

	Substance	ΔH_f° (25°C) kJ mol^{-1}	S° (25°C) J K^{-1} mol^{-1}	ΔG_f° (25°C) kJ mol^{-1}	C_P (25°C) J K^{-1} mol^{-1}
	$HCN(g)$	135.1	201.67	124.7	35.86
	$HCN(aq)$	107.1	124.7	119.7	—
	$CN^-(aq)$	150.6	94.1	172.4	—
	$CH_3NH_2(g)$	−22.97	243.30	32.09	53.1
	$CO(NH_2)_2(s)$	−333.51	104.49	−197.44	93.14
	$Si(s)$	0	18.83	0	20.00
	$Si(g)$	455.6	167.86	411.3	22.25
	$SiC(s)$	−65.3	16.61	−62.8	26.86
	$SiO_2(s$, quartz)	−910.94	41.84	−856.67	44.43
	$SiO_2(s$, cristobalite)	−909.48	42.68	−855.43	44.18
	$Ge(s)$	0	31.09	0	23.35
	$Ge(g)$	376.6	335.9	167.79	30.73
	$Sn(s$, white)	0	51.55	0	26.99
	$Sn(s$, gray)	−2.09	44.14	0.13	25.77
	$Sn(g)$	302.1	168.38	267.3	21.26
	$SnO(s)$	−285.8	56.5	−256.9	44.31
	$SnO_2(s)$	−580.7	52.3	−519.6	52.59
	$Sn(OH)_2(s)$	−561.1	155	−491.7	—
	$Pb(s)$	0	64.81	0	26.44
	$Pb(g)$	195.0	161.9	175.26	20.79
	$Pb^{2+}(aq)$	−1.7	10.5	−24.43	—
	$PbO(s$, yellow)	−217.32	68.70	−187.91	45.77
	$PbO(s$, red)	−218.99	66.5	−188.95	45.81
	$PbO_2(s)$	−277.4	68.6	−217.36	64.64
	$PbS(s)$	−100.4	91.2	−98.7	49.50
	$PbI_2(s)$	−175.48	174.85	−173.64	77.36
	$PbSO_4(s)$	−919.94	148.57	−813.21	103.21
V	$N_2(g)$	0	191.50	0	29.12
	$N(g)$	472.70	153.19	455.58	20.79
	$NH_3(g)$	−46.11	192.34	−16.48	35.06
	$NH_3(aq)$	−80.29	111.3	−26.50	—
	$NH_4^+(aq)$	−132.51	113.4	−79.31	79.9
	$N_2H_4(\ell)$	50.63	121.21	149.24	98.87
	$N_2H_4(aq)$	34.31	138	128.1	—
	$NO(g)$	90.25	210.65	86.55	29.84
	$NO_2(g)$	33.18	239.95	51.29	37.20
	$NO_2^-(aq)$	−104.6	123.0	−32.2	−97.5
	$NO_3^-(aq)$	−205.0	146.4	−108.74	−86.6
	$N_2O(g)$	82.05	219.74	104.18	38.45
	$N_2O_4(g)$	9.16	304.18	97.82	77.28
	$N_2O_5(s)$	−43.1	178.2	113.8	143.1
	$HNO_2(g)$	−79.5	254.0	−46.0	45.6
	$HNO_3(\ell)$	−174.10	155.49	−80.76	109.87
	$NH_4NO_3(s)$	−365.56	151.08	−184.02	139.3
	$NH_4Cl(s)$	−314.43	94.6	−202.97	84.1
	$(NH_4)_2SO_4(s)$	−1180.85	220.1	−901.90	187.49
	$P(s$, white)	0	41.09	0	23.84
	$P(s$, red)	−17.6	22.80	−12.1	21.21
	$P(g)$	314.64	163.08	278.28	20.79
	$P_2(g)$	144.3	218.02	103.7	32.05
	$P_4(g)$	58.91	279.87	24.47	67.15
	$PH_3(g)$	5.4	210.12	13.4	37.11
	$H_3PO_4(s)$	−1279.0	110.50	−1119.2	106.06
	$H_3PO_4(aq)$	−1288.34	158.2	−1142.54	—
	$H_2PO_4^-(aq)$	−1296.29	90.4	−1130.28	—
	$HPO_4^{2-}(aq)$	−1292.14	−33.5	−1089.15	—
	$PO_4^{3-}(aq)$	−1277.4	−222	−1018.7	—

continued

	Substance	**ΔH_f° (25°C)** **kJ mol^{-1}**	**S° (25°C)** **J K^{-1} mol^{-1}**	**ΔG_f° (25°C)** **kJ mol^{-1}**	**C_P (25°C)** **J K^{-1} mol^{-1}**
	PCl_3(*g*)	−287.0	311.67	−267.8	71.84
	PCl_5(*g*)	−374.9	364.47	−305.0	112.80
	As(*s*, gray)	0	35.1	0	24.64
	As(*g*)	302.5	174.10	261.0	20.79
	As_2(*g*)	222.2	239.3	171.9	35.00
	As_4(*g*)	143.9	314	92.4	—
	AsH_3(*g*)	66.44	222.67	68.91	38.07
	As_4O_6(*s*)	−1313.94	214.2	−1152.53	191.29
	Sb(*s*)	0	45.69	0	25.33
	Sb(*g*)	262.3	180.16	222.1	20.79
	Bi(*s*)	0	56.74	0	25.52
	Bi(*g*)	207.1	186.90	168.2	20.79
VI	O_2(*g*)	0	205.03	0	29.36
	O(*g*)	249.17	160.95	231.76	21.91
	O_3(*g*)	142.7	238.82	163.2	39.20
	OH^-(*aq*)	−229.99	−10.75	−157.24	−148.5
	H_2O(ℓ)	−285.83	69.91	−237.18	75.29
	H_2O(*g*)	−241.82	188.72	−228.59	35.58
	H_2O_2(ℓ)	−187.78	109.6	−120.42	89.1
	H_2O_2(*aq*)	−191.17	143.9	−134.03	—
	S(*s*, rhombic)	0	31.80	0	22.64
	S(*s*, monoclinic)	0.30	32.6	0.096	—
	S(*g*)	278.80	167.71	238.28	23.67
	S_8(*g*)	102.30	430.87	49.66	156.44
	H_2S(*g*)	−20.63	205.68	−33.56	34.23
	H_2S(*aq*)	−39.7	121	−27.83	—
	HS^-(*aq*)	−17.6	62.8	12.08	—
	SO(*g*)	6.26	221.84	−19.87	30.17
	SO_2(*g*)	−296.83	248.11	−300.19	39.87
	SO_3(*g*)	−395.72	256.65	−371.08	50.67
	H_2SO_3(*aq*)	−608.81	232.2	−537.81	—
	HSO_3^-(*aq*)	−626.22	139.7	−527.73	—
	SO_3^{2-}(*aq*)	−635.5	−29	−486.5	—
	H_2SO_4(ℓ)	−813.99	156.90	−690.10	138.91
	HSO_4^-(*aq*)	−887.34	131.8	−755.91	−84
	SO_4^{2-}(*aq*)	−909.27	20.1	−744.53	−293
	SF_6(*g*)	−1209	291.71	−1105.4	97.28
	Se(*s*, black)	0	42.44	0	25.36
	Se(*g*)	227.07	176.61	187.06	20.82
VII	F_2(*g*)	0	202.67	0	31.30
	F(*g*)	78.99	158.64	61.94	22.74
	F^-(*aq*)	−332.63	−13.8	−278.79	−106.7
	HF(*g*)	−271.1	173.67	−273.2	29.13
	HF(*aq*)	−320.08	88.7	−296.82	—
	XeF_4(*s*)	−261.5	—	—	—
	Cl_2(*g*)	0	222.96	0	33.91
	Cl(*g*)	121.68	165.09	105.71	21.84
	Cl^-(*aq*)	−167.16	56.5	−131.23	−136.4
	HCl(*g*)	−92.31	186.80	−95.30	29.12
	ClO^-(*aq*)	−107.1	42	−36.8	—
	ClO_2(*g*)	102.5	256.73	120.5	41.97
	ClO_2^-(*aq*)	−66.5	101.3	17.2	—
	ClO_3^-(*aq*)	−103.97	162.3	−7.95	—
	ClO_4^-(*aq*)	−129.33	182.0	−8.52	—
	Cl_2O(*g*)	80.3	266.10	97.9	45.40
	HClO(*aq*)	−120.9	142	−79.9	—

continued

	Substance	ΔH_f° (25°C) kJ mol^{-1}	S° (25°C) J K^{-1} mol^{-1}	ΔG_f° (25°C) kJ mol^{-1}	C_P (25°C) J K^{-1} mol^{-1}
	$ClF_3(g)$	−163.2	281.50	−123.0	63.85
	$Br_2(\ell)$	0	152.23	0	75.69
	$Br_2(g)$	30.91	245.35	3.14	36.02
	$Br_2(aq)$	−2.59	130.5	3.93	—
	$Br(g)$	111.88	174.91	82.41	20.79
	$Br^-(aq)$	−121.55	82.4	−103.96	−141.8
	$HBr(g)$	−36.40	198.59	−53.43	29.14
	$BrO_3^-(aq)$	−67.07	161.71	18.60	—
	$I_2(s)$	0	116.14	0	54.44
	$I_2(g)$	62.44	260.58	19.36	36.90
	$I_2(aq)$	22.6	137.2	16.40	—
	$I(g)$	106.84	180.68	70.28	20.79
	$I^-(aq)$	−55.19	111.3	−51.57	−142.3
	$I_3^-(aq)$	−51.5	239.3	−51.4	—
	$HI(g)$	26.48	206.48	1.72	29.16
	$ICl(g)$	17.78	247.44	−5.44	35.56
	$IBr(g)$	40.84	258.66	3.71	36.44
VIII	$He(g)$	0	126.04	0	20.79
	$Ne(g)$	0	146.22	0	20.79
	$Ar(g)$	0	154.73	0	20.79
	$Kr(g)$	0	163.97	0	20.79
	$Xe(g)$	0	169.57	0	20.79

APPENDIX E

Standard Reduction Potentials at 25°C

Half-Reaction	**$\mathscr{E}°$ (volts)**
$F_2(g) + 2\,e^- \longrightarrow 2\,F^-$	2.87
$H_2O_2 + 2\,H_3O^+ + 2\,e^- \longrightarrow 4\,H_2O$	1.776
$PbO_2(s) + SO_4^{2-} + 4\,H_3O^+ + 2\,e^- \longrightarrow PbSO_4(s) + 6\,H_2O$	1.685
$Au^+ + e^- \longrightarrow Au(s)$	1.68
$MnO_4^- + 4\,H_3O^+ + 3\,e^- \longrightarrow MnO_2(s) + 6\,H_2O$	1.679
$HClO_2 + 2\,H_3O^+ + 2\,e^- \longrightarrow HClO + 3\,H_2O$	1.64
$HClO + H_3O^+ + e^- \longrightarrow \frac{1}{2}\,Cl_2(g) + 2\,H_2O$	1.63
$Ce^{4+} + e^- \longrightarrow Ce^{3+}$ (1 M HNO_3 solution)	1.61
$2\,NO(g) + 2\,H_3O^+ + 2\,e^- \longrightarrow N_2O(g) + 3\,H_2O$	1.59
$BrO_3^- + 6\,H_3O^+ + 5\,e^- \longrightarrow \frac{1}{2}\,Br_2(\ell) + 9\,H_2O$	1.52
$Mn^{3+} + e^- \longrightarrow Mn^{2+}$	1.51
$MnO_4^- + 8\,H_3O^+ + 5\,e^- \longrightarrow Mn^{2+} + 12\,H_2O$	1.491
$ClO_3^- + 6\,H_3O^+ + 5\,e^- \longrightarrow \frac{1}{2}\,Cl_2(g) + 9\,H_2O$	1.47
$PbO_2(s) + 4\,H_3O^+ + 2\,e^- \longrightarrow Pb^{2+} + 6\,H_2O$	1.46
$Au^{3+} + 3\,e^- \longrightarrow Au(s)$	1.42
$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-$	1.3583
$Cr_2O_7^{2-} + 14\,H_3O^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 21\,H_2O$	1.33
$O_3(g) + H_2O + 2\,e^- \longrightarrow O_2 + 2\,OH^-$	1.24
$O_2(g) + 4\,H_3O^+ + 4\,e^- \longrightarrow 6\,H_2O$	1.229
$MnO_2(s) + 4\,H_3O^+ + 2\,e^- \longrightarrow Mn^{2+} + 6\,H_2O$	1.208
$ClO_4^- + 2\,H_3O^+ + 2\,e^- \longrightarrow ClO_3 + 3\,H_2O$	1.19
$Br_2(\ell) + 2\,e^- \longrightarrow 2\,Br^-$	1.065
$NO_3^- + 4\,H_3O^+ + 3\,e^- \longrightarrow NO(g) + 6\,H_2O$	0.96
$2\,Hg^{2+} + 2\,e^- \longrightarrow Hg_2^{2+}$	0.905
$Ag^+ + e^- \longrightarrow Ag(s)$	0.7996
$Hg_2^{2+} + 2\,e^- \longrightarrow 2\,Hg(\ell)$	0.7961
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	0.770
$O_2(g) + 2\,H_3O^+ + 2\,e^- \longrightarrow H_2O_2 + 2\,H_2O$	0.682
$BrO_3^- + 3\,H_2O + 6\,e^- \longrightarrow Br^- + 6\,OH^-$	0.61
$MnO_4^- + 2\,H_2O + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-$	0.588
$I_2(s) + 2\,e^- \longrightarrow 2\,I^-$	0.535
$Cu^+ + e^- \longrightarrow Cu(s)$	0.522
$O_2(g) + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^-$	0.401
$Cu^{2+} + 2\,e^- \longrightarrow Cu(s)$	0.3402
$PbO_2(s) + H_2O + 2\,e^- \longrightarrow PbO(s) + 2\,OH^-$	0.28
$Hg_2Cl_2(s) + 2\,e^- \longrightarrow 2\,Hg(\ell) + 2\,Cl^-$	0.2682
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-$	0.2223
$SO_4^{2-} + 4\,H_3O^+ + 2\,e^- \longrightarrow H_2SO_3 + 5\,H_2O$	0.20

continued

Half-Reaction	$\mathscr{E}^\circ$ (volts)
$Cu^{2+} + e^- \longrightarrow Cu^+$	0.158
$S_4O_6^{2-} + 2\ e^- \longrightarrow 2\ S_2O_3^{2-}$	0.0895
$NO_3^- + H_2O + 2\ e^- \longrightarrow NO_2^- + 2\ OH^-$	0.01
$2\ H_3O^+ + 2\ e^- \longrightarrow H_2(g) + 2\ H_2O(\ell)$	0.000 exactly
$Pb^{2+} + 2\ e^- \longrightarrow Pb(s)$	−0.1263
$Sn^{2+} + 2\ e^- \longrightarrow Sn(s)$	−0.1364
$Ni^{2+} + 2\ e^- \longrightarrow Ni(s)$	−0.23
$Co^{2+} + 2\ e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2\ e^- \longrightarrow Pb(s) + SO_4^{2-}$	−0.356
$Mn(OH)_3(s) + e^- \longrightarrow Mn(OH)_2(s) + OH^-$	−0.40
$Cd^{2+} + 2\ e^- \longrightarrow Cd(s)$	−0.4026
$Fe^{2+} + 2\ e^- \longrightarrow Fe(s)$	−0.409
$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	−0.424
$Fe(OH)_3(s) + e^- \longrightarrow Fe(OH)_2(s) + OH^-$	−0.56
$PbO(s) + H_2O + 2\ e^- \longrightarrow Pb(s) + 2\ OH^-$	−0.576
$2\ SO_3^{2-} + 3\ H_2O + 4\ e^- \longrightarrow S_2O_3^{2-} + 6\ OH^-$	−0.58
$Ni(OH)_2(s) + 2\ e^- \longrightarrow Ni(s) + 2\ OH^-$	−0.66
$Co(OH)_2(s) + 2\ e^- \longrightarrow Co(s) + 2\ OH^-$	−0.73
$Cr^{3+} + 3\ e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+} + 2\ e^- \longrightarrow Zn(s)$	−0.7628
$2\ H_2O + 2\ e^- \longrightarrow H_2(g) + 2\ OH^-$	−0.8277
$Cr^{2+} + 2\ e^- \longrightarrow Cr(s)$	−0.905
$SO_4^{2-} + H_2O + 2\ e^- \longrightarrow SO_3^{2-} + 2\ OH^-$	−0.92
$Mn^{2+} + 2\ e^- \longrightarrow Mn(s)$	−1.029
$Mn(OH)_2(s) + 2\ e^- \longrightarrow Mn(s) + 2\ OH^-$	−1.47
$Al^{3+} + 3\ e^- \longrightarrow Al(s)$	−1.706
$Sc^{3+} + 3\ e^- \longrightarrow Sc(s)$	−2.08
$Ce^{3+} + 3\ e^- \longrightarrow Ce(s)$	−2.335
$La^{3+} + 3\ e^- \longrightarrow La(s)$	−2.37
$Mg^{2+} + 2\ e^- \longrightarrow Mg(s)$	−2.375
$Mg(OH)_2(s) + 2\ e^- \longrightarrow Mg(s) + 2\ OH^-$	−2.69
$Na^+ + e^- \longrightarrow Na(s)$	−2.7109
$Ca^{2+} + 2\ e^- \longrightarrow Ca(s)$	−2.76
$Ba^{2+} + 2\ e^- \longrightarrow Ba(s)$	−2.90
$K^+ + e^- \longrightarrow K(s)$	−2.925
$Li^+ + e^- \longrightarrow Li(s)$	−3.045

All voltages are standard reduction potentials (relative to the standard hydrogen electrode) at 25°C and 1 atm pressure. All species are in aqueous solution unless otherwise indicated.

APPENDIX F

Physical Properties of the Elements

Hydrogen and the Alkali Metals (Group I Elements)

	Hydrogen	Lithium	Sodium	Potassium	Rubidium	Cesium	Francium
Atomic number	1	3	11	19	37	55	87
Atomic mass	1.00794	6.941	22.98976928	39.0983	85.4678	132.9054519	(223.0197)
Melting point (°C)	−259.14	180.54	97.81	63.65	38.89	28.40	25
Boiling point (°C)	−252.87	1347	903.8	774	688	678.4	677
Density at 25°C (g cm^{-3})	0.070 (−253°C)	0.534	0.971	0.862	1.532	1.878	
Color	Colorless	Silver	Silver	Silver	Silver	Silver	
Ground-state electron configuration	$1s^1$	$[\mathrm{He}]2s^1$	$[\mathrm{Ne}]3s^1$	$[\mathrm{Ar}]4s^1$	$[\mathrm{Kr}]5s^1$	$[\mathrm{Xe}]6s^1$	$[\mathrm{Rn}]7s^1$
Ionization energy[†]	1312.0	520.2	495.8	418.8	403.0	375.7	≈400
Electron affinity[†]	72.770	59.63	52.867	48.384	46.884	45.505	est. 44
Electronegativity	2.20	0.98	0.93	0.82	0.82	0.79	0.70
Ionic radius (Å)	1.46(H$^-$)	0.68	0.98	1.33	1.48	1.67	≈1.8
Atomic radius (Å)	0.37	1.52	1.86	2.27	2.47	2.65	≈2.7
Enthalpy of fusion[†]	0.1172	3.000	2.602	2.335	2.351	2.09	
Enthalpy of vaporization[†]	0.4522	147.1	97.42	89.6	76.9	67.8	
Bond enthalpy of M$_2$[†]	436	102.8	72.6	54.8	51.0	44.8	
Standard reduction potential (volts)	0	−3.045	−2.7109	−2.924	−2.925	−2.923	≈2.9
	H^+/H_2	Li^+/Li	Na^+/Na	K^+/K	Rb^+/Rb	Cs^+/Cs	Fr^+/Fr

[†] In kilojoules per mole.

The Alkaline-Earth Metals (Group II Elements)

	Beryllium	Magnesium	Calcium	Strontium	Barium	Radium
Atomic number	4	12	20	38	56	88
Atomic mass	9.012182	24.3050	40.078	87.62	137.327	(226.0254)
Melting point (°C)	1283	648.8	839	769	725	700
Boiling point (°C)	2484	1105	1484	1384	1640	
Density at 25°C (g cm^{-3})	1.848	1.738	1.55	2.54	3.51	5
Color	Gray	Silver	Silver	Silver	Silver-yellow	Silver
Ground-state electron configuration	$[\mathrm{He}]2s^2$	$[\mathrm{Ne}]3s^2$	$[\mathrm{Ar}]4s^2$	$[\mathrm{Kr}]5s^2$	$[\mathrm{Xe}]6s^2$	$[\mathrm{Rn}]7s^2$
Ionization energy[†]	899.4	737.7	589.8	549.5	502.9	509.3
Electron affinity[†]	<0	<0	2.0	4.6	13.95	>0
Electronegativity	1.57	1.31	1.00	0.95	0.89	0.90
Ionic radius (Å)	0.31	0.66	0.99	1.13	1.35	1.43
Atomic radius (Å)	1.13	1.60	1.97	2.15	2.17	2.23
Enthalpy of fusion[†]	11.6	8.95	8.95	9.62	7.66	7.15
Enthalpy of vaporization[†]	297.6	127.6	154.7	154.4	150.9	136.7
Bond enthalpy of M_2[†]	9.46					
Standard reduction potential (volts)	−1.70	−2.375	−2.76	−2.89	−2.90	−2.916
	Be^{2+}/Be	Mg^{2+}/Mg	Ca^{2+}/Ca	Sr^{2+}/Sr	Ba^{2+}/Ba	Ra^{2+}/Ra

Group III Elements

	Boron	Aluminum	Gallium	Indium	Thallium
Atomic number	5	13	31	49	81
Atomic mass	10.811	26.9815386	69.723	114.818	204.3833
Melting point (°C)	2300	660.37	29.78	156.61	303.5
Boiling point (°C)	3658	2467	2403	2080	1457
Density at 25°C (g cm^{-3})	2.34	2.702	5.904	7.30	11.85
Color	Yellow	Silver	Silver	Silver	Blue-white
Ground-state electron configuration	$[\mathrm{He}]2s^2 2p^1$	$[\mathrm{Ne}]3s^2 3p^1$	$[\mathrm{Ar}]3d^{10}4s^2 4p^1$	$[\mathrm{Kr}]4d^{10}5s^2 5p^1$	$[\mathrm{Xe}]4f^{14}5d^{10}6s^2 6p^1$
Ionization energy[†]	800.6	577.6	578.8	558.3	589.3
Electron affinity[†]	26.7	42.6	29	29	≈ 20
Electronegativity	2.04	1.61	1.81	1.78	1.83
Ionic radius (Å)	0.23 (+3)	0.51 (+3)	0.62 (+3)	0.81 (+3)	0.95 (+3)
Atomic radius (Å)	0.88	1.43	1.22	1.63	1.70
Enthalpy of fusion[†]	22.6	10.75	5.59	3.26	4.08
Enthalpy of vaporization[†]	508	291	272	243	182
Bond enthalpy of M_2[†]	295	167	116	106	≈ 63
Standard reduction potential (volts)	−0.890	−1.706	−0.560	−0.338	0.719
	$B(OH)_3/B$	Al^{3+}/Al	Ga^{3+}/Ga	In^{3+}/In	Tl^{3+}/Tl

[†] In kilojoules per mole.

Group IV Elements

	Carbon	Silicon	Germanium	Tin	Lead
Atomic number	6	14	32	50	82
Atomic mass	12.0107	28.0855	72.64	118.710	207.2
Melting point (°C)	3550	1410	937.4	231.9681	327.502
Boiling point (°C)	4827	2355	2830	2270	1740
Density at 25°C (g cm^{-3})	2.25 (gr)	2.33	5.323	5.75 (gray)	11.35
	3.51 (dia)			7.31 (white)	
Color	Black (gr)	Gray	Gray-white	Silver	Blue-white
	Colorless (dia)				
Ground-state electron configuration	$[He]2s^{2}2p^{2}$	$[Ne]3s^{2}3p^{2}$	$[Ar]3d^{10}4s^{2}4p^{2}$	$[Kr]4d^{10}5s^{2}5p^{2}$	$[Xe]4f^{14}5d^{10}6s^{2}6p^{2}$
Ionization energy[†]	1086.4	786.4	762.2	708.6	715.5
Electron affinity[†]	121.85	133.6	≈120	≈120	35.1
Electronegativity	2.55	1.90	2.01	1.88	2.10
Ionic radius (Å)	0.15 (+4)	0.42 (+4)	0.53 (+4)	0.71 (+4)	0.84 (+4)
	2.60 (−4)	2.71 (−4)	0.73 (+2)	0.93 (+2)	1.20 (+2)
			2.72 (−4)		
Atomic radius (Å)	0.77	1.17	1.22	1.40	1.75
Enthalpy of fusion[†]	105.0	50.2	34.7	6.99	4.774
Enthalpy of vaporization[†]	718.9	359	328	302	195.6
Bond enthalpy of M_2[†]	178	317	280	192	61
Standard reduction potential (volts)			−0.13	−0.1364	−0.1263
			H_2GeO_3,H^+/Ge	Sn^{2+}/Sn	Pb^{2+}/Pb

Group V Elements

	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Atomic number	7	15	33	51	83
Atomic mass	14.00674	30.973762	74.92160	121.760	208.98040
Melting point (°C)	−209.86	44.1	817 (28 atm.)	630.74	271.3
Boiling point (°C)	−195.8	280	613 (subl.)	1750	1560
Density at 25°C (g cm^{-3})	0.808	1.82 (white)	5.727	6.691	9.747
	(−196°C)	2.20 (red)			
Color	Colorless	2.69 (black)	Gray	Blue-white	White
Ground-state electron configuration	$[He]2s^{2}2p^{3}$	$[Ne]3s^{2}3p^{3}$	$[Ar]3d^{10}4s^{2}4p^{3}$	$[Kr]4d^{10}5s^{2}5p^{3}$	$[Xe]4f^{14}5d^{10}6s^{2}6p^{3}$
Ionization energy[†]	1402.3	1011.7	947	833.7	703.3
Electron affinity[†]	−7	72.03	≈80	103	91.3
Electronegativity	3.04	2.19	2.18	2.05	2.02
Ionic radius (Å)	1.71 (−3)	0.44 (+3)	0.46 (+5)	0.62 (+5)	0.96 (+3)
		2.12 (−3)	0.58 (+3)	0.76 (+3)	
			2.22 (−3)	2.45 (−3)	
Atomic radius (Å)	0.70	1.10	1.21	1.41	1.55
Enthalpy of fusion[†]	0.720	6.587	27.72	20.91	10.88
Enthalpy of vaporization[†]	5.608	59.03	334	262.5	184.6
Bond enthalpy of M_2[†]	945	485	383	289	194
Standard reduction potential (volts)	0.96	−0.276	0.234	0.1445	−0.46
	NO_3^-,H^+/NO	H_3PO_4/H_3PO_3	As_2O_3,H^+/As	Sb_2O_3,H^+/Sb	Bi_2O_3,OH^-/Bi

[†] In kilojoules per mole.

The Chalcogens (Group VI Elements)

	Oxygen	Sulfur	Selenium	Tellurium	Polonium
Atomic number	8	16	34	52	84
Atomic mass	15.9994	32.065	78.96	127.60	(208.9824)
Melting point (°C)	−218.4	119.0 (mon.)	217	449.5	254
		112.8 (rhom.)			
Boiling point (°C)	−182.962	444.674	684.9	989.8	962
Density at 25°C (g cm^{-3})	1.14	1.957 (mon.)	4.79	6.24	9.32
	(−183°C)	2.07 (rhom.)			
Color	Pale blue (ℓ)	Yellow	Gray	Silver	Silver-gray
Ground-state electron configuration	$[He]2s^22p^4$	$[Ne]3s^23p^4$	$[Ar]3d^{10}4s^24p^4$	$[Kr]4d^{10}5s^25p^4$	$[Xe]4f^{14}5d^{10}6s^26p^4$
Ionization energy[†]	1313.9	999.6	940.9	869.3	812
Electron affinity[†]	140.97676	200.4116	194.967	190.15	≈180
Electronegativity	3.44	2.58	2.55	2.10	2.00
Ionic radius (Å)	1.40 (−2)	0.29 (+6)	0.42 (+6)	0.56 (+6)	0.67 (+6)
		1.84 (−2)	1.98 (−2)	2.21 (−2)	2.30 (−2)
Atomic radius (Å)	0.66	1.04	1.17	1.43	1.67
Enthalpy of fusion[†]	0.4187	1.411	5.443	17.50	10
Enthalpy of vaporization[†]	6.819	238	207	195	90
Bond enthalpy of M_2[†]	498	429	308	225	
Standard reduction potential (volts)	1.229	−0.508	−0.78	−0.92	≈−1.4
	$O_2,H^+/H_2O$	S/S^{2-}	Se/Se^{2-}	Te/Te^{2-}	Po/Po^{2-}

The Halogens (Group VII Elements)

	Fluorine	Chlorine	Bromine	Iodine	Astatine
Atomic number	9	17	35	53	85
Atomic mass	18.9984032	35.453	79.904	126.90447	(209.9871)
Melting point (°C)	−219.62	−100.98	−7.25	113.5	302
Boiling point (°C)	−188.14	−34.6	58.78	184.35	337
Density at 25°C (g cm^{-3})	1.108	1.367	3.119	4.93	
	(−189°C)	(−34.6°C)			
Color	Yellow	Yellow-green	Deep red	Violet-black	
Ground-state electron configuration	$[He]2s^22p^5$	$[Ne]3s^23p^5$	$[Ar]3d^{10}4s^24p^5$	$[Kr]4d^{10}5s^25p^5$	$[Xe]4f^{14}5d^{10}6s^26p^5$
Ionization energy[†]	1681.0	1251.1	1139.9	1008.4	≈930
Electron affinity[†]	328.0	349.0	324.7	295.2	≈270
Electronegativity	3.98	3.16	2.96	2.66	2.20
Ionic radius (Å)	1.33	1.81	1.96	2.20	≈2.27
Atomic radius (Å)	0.64	0.99	1.14	1.33	1.40
Enthalpy of fusion[†]	0.511	6.410	10.55	15.78	23.9
Enthalpy of vaporization[†]	6.531	20.347	29.56	41.950	
Bond enthalpy of M_2[†]	158	243	193	151	110
Standard reduction potential (volts)	2.87	1.358	1.065	0.535	≈0.2
	F_2/F^-	Cl_2/Cl^-	Br_2/Br^-	I_2/I^-	At_2/At^-

[†] In kilojoules per mole.

The Noble Gases (Group VIII Elements)

	Helium	Neon	Argon	Krypton	Xenon	Radon
Atomic number	2	10	18	36	54	86
Atomic mass	4.002602	20.1797	39.948	83.798	131.293	(222.0176)
Melting point (°C)	−272.2 (26 atm)	−248.67	−189.2	−156.6	−111.9	−71
Boiling point (°C)	−268.934	−246.048	−185.7	−152.30	−107.1	−61.8
Density at 25°C (g cm^{-3})	0.147 (−270.8°C)	1.207 (−246.1°C)	1.40 (−186°C)	2.155 (−152.9°C)	3.52 (−109°C)	4.4 (−52°C)
Color	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
Ground-state electron configuration	$1s^2$	[He]$2s^22p^6$	[Ne]$3s^23p^6$	[Ar]$3d^{10}4s^24p^6$	[Kr]$4d^{10}5s^25p^6$	[Xe]$4f^{14}5d^{10}6s^26p^6$
Ionization energy†	2372.3	2080.6	1520.5	1350.7	1170.4	1037.0
Electron affinity†	<0	<0	<0	<0	<0	<0
Atomic radius (Å)	0.32	0.69	0.97	1.10	1.30	1.45
Enthalpy of fusion†	0.02093	0.3345	1.176	1.637	2.299	2.9
Enthalpy of vaporization†	0.1005	1.741	6.288	9.187	12.643	18.4

†In kilojoules per mole.

The Transition Elements

	Scandium	Yttrium	Lutetium	Titanium	Zirconium	Hafnium
Atomic number	21	39	71	22	40	72
Atomic mass	44.955912	88.90585	174.967	47.867	91.224	178.49
Melting point (°C)	1541	1522	1656	1660	1852	2227
Boiling point (°C)	2831	3338	3315	3287	4504	4602
Density at 25°C (g cm^{-3})	2.989	4.469	9.840	4.54	6.506	13.31
Color	Silver	Silver	Silver	Silver	Gray-white	Silver
Ground-state electron configuration	[Ar]$3d^14s^2$	[Kr]$4d^15s^2$	[Xe]$4f^{14}5d^16s^2$	[Ar]$3d^24s^2$	[Kr]$4d^25s^2$	[Xe]$4f^{14}5d^26s^2$
Ionization energy†	631	616	523.5	658	660	654
Electron affinity†	18.1	29.6	≈50	7.6	41.1	≈0
Electronegativity	1.36	1.22	1.27	1.54	1.33	1.30
Ionic radius (Å)	0.81	0.93	0.848 ($^+$3)	0.68	0.80	0.78
Atomic radius (Å)	1.61	1.78	1.72	1.45	1.59	1.56
Enthalpy of fusion†	11.4	11.4	19.2	18.62	20.9	25.5
Enthalpy of vaporization†	328	425	247	426	590	571
Standard reduction potential (volts)	−2.08 Sc^{3+}/Sc	−2.37 Y^{3+}/Y	−2.30 Lu^{3+}/Lu	−0.86 $TiO_2,H^+/Ti$	−1.43 $ZrO_2,H^+/Zr$	−1.57 $HfO_2,H^+/Hf$

†In kilojoules per mole.

The Transition Elements (cont.)

	Vanadium	Niobium	Tantalum	Chromium	Molybdenum	Tungsten
Atomic number	23	41	73	24	42	74
Atomic mass	50.9415	92.90638	180.94788	51.9961	95.94	183.84
Melting point (°C)	1890	2468	2996	1857	2617	3410
Boiling point (°C)	3380	4742	5425	2672	4612	5660
Density at 25°C (g cm^{-3})	6.11	8.57	16.654	7.18	10.22	19.3
Color	Silver-white	Gray-white	Steel gray	Silver	Silver	Steel gray
Ground-state electron configuration	[Ar]$3d^34s^2$	[Kr]$4d^45s^1$	[Xe]$4f^{14}5d^36s^2$	[Ar]$3d^54s^1$	[Kr]$4d^55s^1$	[Xe]$4f^{14}5d^46s^2$
Ionization energy[†]	650	664	761	652.8	684.9	770
Electron affinity[†]	50.7	86.2	31.1	64.3	72.0	78.6
Electronegativity	1.63	1.60	1.50	1.66	2.16	2.36
Ionic radius (Å)	0.59 (+5)	0.69 (+5)	0.68 (+5)		0.62 (+6)	0.62 (+6)
	0.63 (+4)	0.74 (+4)		0.63 (+3)	0.70 (+4)	0.70 (+4)
	0.74 (+3)			0.89 (+2)		
	0.88 (+2)					
Atomic radius (Å)	1.31	1.43	1.43	1.25	1.36	1.37
Enthalpy of fusion[†]	21.1	26.4		20.9	27.8	35.4
Enthalpy of vaporization[†]	512	722	781	394.7	589.2	819.3
Standard reduction potential (volts)	−1.2	−0.62	−0.71	−0.74	0.0	−0.09
	V^{2+}/V	$Nb_2O_5,H^+/Nb$	$Ta_2O_5,H^+/Ta$	Cr^{3+}/Cr	$H_2MoO_4,H^+/Mo$	$WO_3,H^+/W$

	Manganese	Technetium	Rhenium	Iron	Ruthenium	Osmium
Atomic number	25	43	75	26	44	76
Atomic mass	54.938045	(97.9064)	186.207	55.845	101.07	190.23
Melting point (°C)	1244	2172	3180	1535	2310	3045
Boiling point (°C)	1962	4877	5627	2750	3900	5027
Density at 25°C (g cm^{-3})	7.21	11.50	21.02	7.874	12.41	22.57
Color	Gray-white	Silver-gray	Silver	Gray	White	Blue-white
Ground-state electron configuration	[Ar]$3d^54s^2$	[Kr]$4d^55s^2$	[Xe]$4f^{14}5d^56s^2$	[Ar]$3d^64s^2$	[Kr]$4d^75s^1$	[Xe]$4f^{14}5d^66s^2$
Ionization energy[†]	717.4	702	760	759.3	711	840
Electron affinity[†]	<0	≈53	≈14	15.7	≈100	≈106
Electronegativity	1.55	1.90	1.90	1.90	2.2	2.20
Ionic radius (Å)	0.80 (+2)		0.56 (+7)	0.60 (+3)	0.67 (+4)	0.69 (+6)
			0.27 (+4)	0.72 (+2)		0.88 (+4)
Atomic radius (Å)	1.37	1.35	1.34	1.24	1.32	1.34
Enthalpy of fusion[†]	14.6	23.8	33.1	15.19	26.0	31.8
Enthalpy of vaporization[†]	279	585	778	414	649	678
Standard reduction potential (volts)	−0.183	0.738	0.3	−0.036	0.49	0.85
	Mn^{3+}/Mn	$TcO_4^-,H^+/TcO_2$	Re^{3+}/Re	Fe^{3+}/Fe	Ru^{4+}/Ru^{3+}	$OsO_4,H^+/Os$

[†] In kilojoules per mole.

The Transition Elements (cont.)

	Cobalt	Rhodium	Iridium	Nickel	Palladium	Platinum
Atomic number	27	45	77	28	46	78
Atomic mass	58.933195	102.90550	192.217	58.6934	106.42	195.084
Melting point (°C)	1459	1966	2410	1453	1552	1772
Boiling point (°C)	2870	3727	4130	2732	3140	3827
Density at 25°C (g cm^{-3})	8.9	12.41	22.42	8.902	12.02	21.45
Color	Steel gray	Silver	Silver	Silver	Steel white	Silver
Ground-state electron configuration	$[\mathrm{Ar}]3d^{7}4s^{2}$	$[\mathrm{Kr}]4d^{8}5s^{1}$	$[\mathrm{Xe}]4f^{14}5d^{7}6s^{2}$	$[\mathrm{Ar}]3d^{8}4s^{2}$	$[\mathrm{Kr}]4d^{10}$	$[\mathrm{Xe}]4f^{14}5d^{9}6s^{1}$
Ionization energy†	758	720	880	736.7	805	868
Electron affinity†	63.8	110	151	111.5	51.8	205.1
Electronegativity	1.88	2.28	2.20	1.91	2.20	2.28
Ionic radius (Å)	0.63 (+3)	0.68 (+3)	0.68 (+4)	0.69 (+2)	0.65 (+4)	0.65 (+4)
	0.72 (+2)				0.80 (+2)	0.80 (+2)
Atomic radius (Å)	1.25	1.34	1.36	1.25	1.38	1.37
Enthalpy of fusion†	16.2	21.5	26.4	17.6	17.6	19.7
Enthalpy of vaporization†	373	557	669	428	353	564
Standard reduction potential (volts)	−0.28	1.43	0.1	−0.23	0.83	1.2
	Co^{2+}/Co	Rh^{4+}/Rh^{3+}	$Ir_2O_3/Ir,OH^-$	Ni^{2+}/Ni	Pd^{2+}/Pd	Pt^{2+}/Pt

	Copper	Silver	Gold	Zinc	Cadmium	Mercury
Atomic number	29	47	79	30	48	80
Atomic mass	63.546	107.8682	196.966569	65.409	112.411	200.59
Melting point (°C)	1083.4	961.93	1064.43	419.58	320.9	−38.87
Boiling point (°C)	2567	2212	2807	907	765	356.58
Density at 25°C (g cm^{-3})	8.96	10.50	19.32	7.133	8.65	13.546
Color	Red	Silver	Yellow	Blue-white	Blue-white	Silver
Ground-state electron configuration	$[\mathrm{Ar}]3d^{10}4s^{1}$	$[\mathrm{Kr}]4d^{10}5s^{1}$	$[\mathrm{Xe}]4f^{14}5d^{10}6s^{1}$	$[\mathrm{Ar}]3d^{10}4s^{2}$	$[\mathrm{Kr}]4d^{10}5s^{2}$	$[\mathrm{Xe}]4f^{14}5d^{10}6s^{2}$
Ionization energy†	745.4	731.0	890.1	906.4	867.7	1007.0
Electron affinity†	118.5	125.6	222.749	<0	<0	<0
Electronegativity	1.90	1.93	2.54	1.65	1.69	2.00
Ionic radius (Å)	0.72 (+2)	0.89 (+2)	0.85 (+2)	0.74 (+2)	0.97 (+2)	1.10 (+2)
	0.96 (+1)	1.26 (+1)	1.37 (+1)		1.14 (+1)	1.27 (+1)
Atomic radius (Å)	1.28	1.44	1.44	1.34	1.49	1.50
Enthalpy of fusion†	13.3	11.95	12.36	7.39	6.11	2.300
Enthalpy of vaporization†	304	285	365	131	112	59.1
Standard reduction potential (volts)	0.340	0.800	1.42	−0.763	−0.403	0.796
	Cu^{2+}/Cu	Ag^{+}/Ag	Au^{3+}/Au	Zn^{2+}/Zn	Cd^{2+}/Cd	Hg_2^{2+}/Hg

† In kilojoules per mole.

The Lanthanide Elements

	Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium
Atomic number	57	58	59	60	61	62	63
Atomic mass	138.90547	140.116	140.90765	144.242	(144.9127)	150.36	151.964
Melting point (°C)	921	798	931	1010	≈1080	1072	822
Boiling point (°C)	3457	3257	3212	3127	≈2400	1778	1597
Density at 25°C (g cm^{-3})	6.145	6.657	6.773	6.80	7.22	7.520	5.243
Color	Silver	Gray	Silver	Silver		Silver	Silver
Ground-state electron configuration	$[\mathrm{Xe}]5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{1}5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{3}6s^{2}$	$[\mathrm{Xe}]4f^{4}6s^{2}$	$[\mathrm{Xe}]4f^{5}6s^{2}$	$[\mathrm{Xe}]4f^{6}6s^{2}$	$[\mathrm{Xe}]4f^{7}6s^{2}$
Ionization energy[†]	538.1	528	523	530	536	543	547
Electron affinity[†]	50	est. 50					
Electronegativity	1.10	1.12	1.13	1.14		1.17	
Ionic radius (Å)	1.15	0.92 (+4) 1.034 (+3)	0.90 (+4) 1.013 (+3)	0.995 (+3)	0.979 (+3)	0.964 (+3)	0.950 (+3) 1.09 (+2)
Atomic radius (Å)	1.87	1.82	1.82	1.81	1.81	1.80	2.00
Enthalpy of fusion[†]	5.40	5.18	6.18	7.13	12.6	8.91	(10.5)
Enthalpy of vaporization[†]	419	389	329	324		207	172
Standard reduction potential (volts)	−2.37 La^{3+}/La	−2.335 Ce^{3+}/Ce	−2.35 Pr^{3+}/Pr	−2.32 Nd^{3+}/Nd	−2.29 Pm^{3+}/Pm	−2.30 Sm^{3+}/Sm	−1.99 Eu^{3+}/Eu

	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium
Atomic number	64	65	66	67	68	69	70
Atomic mass	157.25	158.92535	162.500	164.93032	167.259	168.93421	173.04
Melting point (°C)	1311	1360	1409	1470	1522	1545	824
Boiling point (°C)	3233	3041	2335	2720	2510	1727	1193
Density at 25°C (g cm^{-3})	7.900	8.229	8.550	8.795	9.066	9.321	6.965
Color	Silver	Silver-gray	Silver	Silver	Silver	Silver	Silver
Ground-state electron configuration	$[\mathrm{Xe}]4f^{7}5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{9}6s^{2}$	$[\mathrm{Xe}]4f^{10}6s^{2}$	$[\mathrm{Xe}]4f^{11}6s^{2}$	$[\mathrm{Xe}]4f^{12}6s^{2}$	$[\mathrm{Xe}]4f^{13}6s^{2}$	$[\mathrm{Xe}]4f^{14}6s^{2}$
Ionization energy[†]	592	564	572	581	589	596.7	603.4
Electron affinity[†]	est. 50						
Electronegativity	1.20		1.22	1.23	1.24	1.25	
Ionic radius (Å)	0.938 (+3)	0.84 (+4) 0.923 (+3)	0.908 (+3)	0.894 (+3)	0.881 (+3)	0.869 (+3)	0.858 (+3) 0.93 (+2)
Atomic radius (Å)	1.79	1.76	1.75	1.74	1.73	1.72	1.94
Enthalpy of fusion[†]	15.5	16.3	17.2	17.2	17.2	18.2	9.2
Enthalpy of vaporization[†]	301	293	165	285	280	240	165
Standard reduction potential (volts)	−2.28 Gd^{3+}/Gd	−2.31 Tb^{3+}/Tb	−2.29 Dy^{3+}/Dy	−2.33 Ho^{3+}/Ho	−2.32 Er^{3+}/Er	−2.32 Tm^{3+}/Tm	−2.22 Yb^{3+}/Yb

[†] In kilojoules per mole.

The Actinide Elements

	Actinium	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium
Atomic number	89	90	91	92	93	94	95
Atomic mass	(227.0277)	232.0381	231.0359	238.0289	(237.0482)	(244.0642)	(243.0614)
Melting point (°C)	1050	1750	1600	1132.3	640	624	994
Boiling point (°C)	3200	4790		3818	2732	3232	2607
Density at 25°C (g cm^{-3})	10.07	11.72	15.37	18.95	20.25	19.84	13.67
Color	Silver	Silver	Silver	Silver	Silver	Silver	Silver
Ground-state electron configuration	[Rn]$6d^1 7s^2$	[Rn]$6d^2 7s^2$	[Rn]$5f^2 6d^1 7s^2$	[Rn]$5f^3 6d^1 7s^2$	[Rn]$5f^4 6d^1 7s^2$	[Rn]$5f^6 7s^2$	[Rn]$5f^7 7s^2$
Ionization energy[†]	499	587	568	587	597	585	578
Electronegativity	1.1	1.3	1.5	1.38	1.36	1.28	1.3
Ionic radius (Å)	1.11 (+3)	0.99 (+4)	0.89 (+5) 0.96 (+4) 1.05 (+3)	0.80 (+6) 0.93 (+4) 1.03 (+3)	0.71 (+7) 0.92 (+4) 1.01 (+3)	0.90 (+4) 1.00 (+3)	0.89 (+4) 0.99 (+3)
Atomic radius (Å)	1.88	1.80	1.61	1.38	1.30	1.51	1.84
Enthalpy of fusion[†]	14.2	18.8	16.7	12.9	9.46	3.93	14.4
Enthalpy of vaporization[†]	293	575	481	536	337	348	238
Standard reduction potential (volts)	−2.6 Ac^{3+}/Ac	−1.90 Th^{4+}/Th	−1.0 $PaO_2^+, H^+/Pa$	−1.8 U^{3+}/U	−1.9 Np^{3+}/U	−2.03 Pu^{3+}/Pu	−2.32 Am^{3+}/Am

	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium
Atomic number	96	97	98	99	100	101	102
Atomic mass	(247.0703)	(247.0703)	(251.0796)	(252.0830)	(257.0951)	(258.0984)	(259.1011)
Melting point (°C)	1340						
Boiling point (°C)							
Density at 25°C (g cm^{-3})	13.51	14					
Color	Silver	Silver	Silver	Silver			
Ground-state electron configuration	[Rn]$5f^7 6d^1 7s^2$	[Rn]$5f^9 7s^2$	[Rn]$5f^{10} 7s^2$	[Rn]$5f^{11} 7s^2$	[Rn]$5f^{12} 7s^2$	[Rn]$5f^{13} 7s^2$	[Rn]$5f^{14} 7s^2$
Ionization energy[†]	581	601	608	619	627	635	642
Electronegativity	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Ionic radius (Å)	0.88 (+4) 1.01 (+3) 1.19 (+2)	0.87 (+4) 1.00 (+3) 1.18 (+2)	0.86 (+4) 0.99 (+3) 1.17 (+2)	0.85 (+4) 0.98 (+3) 1.16 (+2)	0.84 (+4) 0.97 (+3) 1.15 (+2)	0.84 (+4) 0.96 (+3) 1.14 (+2)	0.83 (+4) 0.95 (+3) 1.13 (+2)
Standard reduction potential (volts)	−2.06 Cm^{3+}/Cm	−1.05 Bk^{3+}/Bk	−1.93 Cf^{3+}/Cf	−2.0 Es^{3+}/Es	−1.96 Fm^{3+}/Fm	−1.7 Md^{3+}/Md	−1.2 No^{3+}/No

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[†] In kilojoules per mole.

The Transactinide Elements[†]

	Lawrencium	Rutherfordium	Dubnium	Seaborgium	Bohrium	Hassium	Meitnerium
Atomic number	103	104	105	106	107	108	109
Atomic mass	(262)	(261)	(262)	(263)	(262)	(265)	(266)
Melting point (°C)	1600						
Ground-state electron configuration	[Rn]$5f^{14} 7s^2 7p^1$	[Rn]$5f^{14} 6d^2 7s^2$	[Rn]$5f^{14} 6d^3 7s^2$	[Rn]$5f^{14} 6d^4 7s^2$	[Rn]$5f^{14} 6d^5 7s^2$	[Rn]$5f^{14} 6d^6 7s^2$	[Rn]$5f^{14} 6d^7 7s^2$
Ionization energy		490	640	730	660	750	840

[†] All missing data are unknown.

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APPENDIX G

Answers to Odd-Numbered Problems

CHAPTER 1

1. Mercury is an element; water and sodium chloride are compounds. The other materials are mixtures: seawater and air are homogeneous; table salt and wood are heterogeneous. Mayonnaise appears homogeneous to the naked eye, but under magnification shows itself as water droplets suspended in oil.

3. Substances

5. 16.9 g

7. (a) 2.005 and 1.504 g
(b) 2.005/1.504 = 1.333 = 4/3; SiN (or a multiple)

9. 2, 3, 4, 5

11. (a) HO (or any multiple, such as H_2O_2)
(b) All would give H_2 and O_2 in 1:1 ratio.

13. 2.0 L N_2O, 3.0 L O_2

15. 28.086

17. 11.01

19. (a) 145/94 = 1.54 (b) 94 electrons

21. 95 protons, 146 neutrons, 95 electrons

CHAPTER 2

1. 2.107298×10^{-22} g

3. (a) 283.89 (b) 115.36 (c) 164.09 (d) 158.03 (e) 132.13

5. The total count of 2.52×10^9 atoms of gold has a mass of only 8.3×10^{-13} g, which is far too small to detect with a balance.

7. 1.041 mol

9. 2540 cm^3 = 2.54 L

11. 7.03×10^{23} atoms

13. Pt: 47.06%; F: 36.67%; Cl: 8.553%; O: 7.720%

15. N_4H_6, H_2O, LiH, $C_{12}H_{26}$

17. 0.225%

19. $Zn_3P_2O_8$

21. Fe_3Si_7

23. BaN, Ba_3N_2

25. (a) 0.923 g C, 0.077 g H
(b) No
(c) 92.3% C, 7.7% H
(d) CH

27. C_4F_8

29. (a) 62.1
  (b) 6
  (c) 56
  (d) Si (atomic mass 28.1), N (atomic mass 14.0)
  (e) Si_2H_6

31. (a) $3\ H_2 + N_2 \longrightarrow 2\ NH_3$
  (b) $2\ K + O_2 \longrightarrow K_2O_2$
  (c) $PbO_2 + Pb + 2\ H_2SO_4 \longrightarrow 2\ PbSO_4 + 2\ H_2O$
  (d) $2\ BF_3 + 3\ H_2O \longrightarrow B_2O_3 + 6\ HF$
  (e) $2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2$
  (f) $CH_3COOH + 2\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O$
  (g) $2\ K_2O_2 + 2\ H_2O \longrightarrow 4\ KOH + O_2$
  (h) $3\ PCl_5 + 5\ AsF_3 \longrightarrow 3\ PF_5 + 5\ AsCl_3$

33. (a) 12.06 g (b) 1.258 g (c) 4.692 g

35. 7.83 g $K_2Zn_3[Fe(CN)_6]_2$

37. 0.134 g SiO_2

39. 1.18×10^3 g

41. 418 g KCl; 199 g Cl_2

43. (a) 58.8 (b) Probably nickel (Ni)

45. 42.49% NaCl, 57.51% KCl

47. 14.7 g NH_4Cl, 5.3 g NH_3

49. 303.0 g Fe; 83.93%

CHAPTER 3

1. Melting point 1250°C (obs. 1541°C), boiling point 2386°C (obs. 2831°C), density 3.02 g cm^{-3} (obs. 2.99)

3. SbH_3, HBr, SnH_4, H_2Se

5. (a) $F(r) = 7.1999 \times 10^{-9}$ N
  (b) $V(r) = 8.984741$ eV

7. (a) -8.63994×10^{-8} N
  (b) -17.96933 eV
  (c) 1.951188×10^7 m s^{-1}

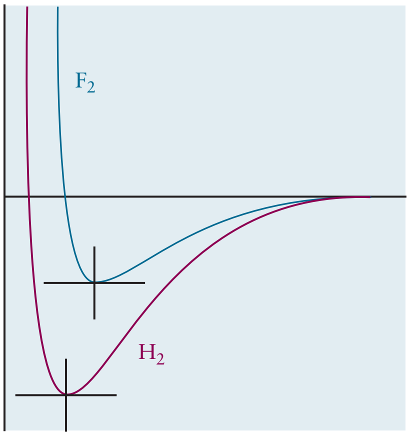
9. (a) Sr (b) Rn (c) Xe (d) Sr

11. Using data for Be from Table 3.1, calculate $\log(I_n)$ for $n = 1, 2, 3$, and 4. The graph of $\log(I_n)$ versus n shows a dramatic increase between $n = 2$ and $n = 3$, suggesting two easily removed electrons outside a stable helium-like inner shell containing two electrons.

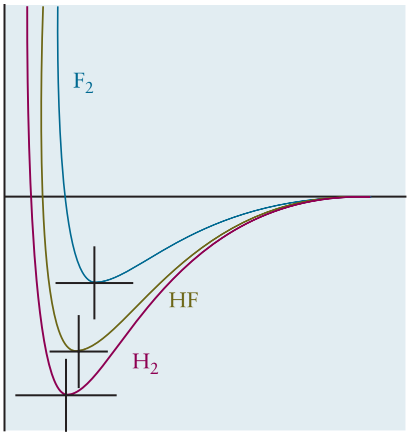
13. (a) Cs (b) F (c) K (d) At

15. K < Si < S < O < F

17.



19.



21. (a) 86 e^- (8 valence, 78 core)
(b) 37 e^- (1 valence, 36 core)
(c) 36 e^- (8 valence, 28 core)
(d) 52 e^- (6 valence, 46 core)

23. $K(g) + Cl(g) \longrightarrow K^+(g) + Cl^-(g) \qquad \Delta E = 70 \text{ kJ mol}^{-1}$
$K(g) + Cl(g) \longrightarrow K^-(g) + Cl^+(g) \qquad \Delta E = 1203 \text{ kJ mol}^{-1}$

25. 450 kJ mol^{-1}

27. The As—H bond length will lie between 1.42 and 1.71 Å (observed: 1.52 Å). SbH_3 will have the weakest bond.

29. Bond lengths are often shorter than the sum of atomic radii in polar molecules because of the electrostatic attraction between the oppositely charged ends of the dipole. Such shortening is slight in HI, indicating that it is not very polar.

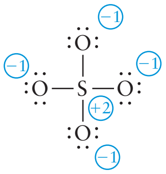
31. Most polar: N—P > C—N > N—O > N—N :least polar

33. (a) CI_4 (b) OF_2 (c) SiH_4

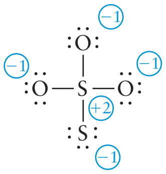
35. ClO, 16%; KI, 74%; TlCl, 38%; InCl, 33%

37. HF, 40%; HCl, 19%; HBr, 14%; HI, 8%; CsF, 87%

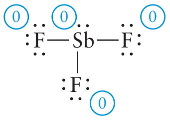
39. (a)



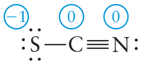
(b)



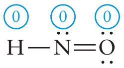
(c)

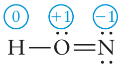


(d)



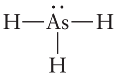
41. The first is favored.



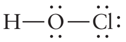


43. (a) Group IV, CO_2 (b) Group VII, Cl_2O_7
(c) Group V, NO_2^- (d) Group VI, HSO_4^-

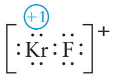
45. (a)



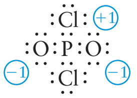
(b)



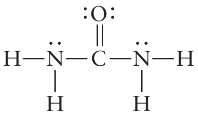
(c)



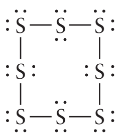
(d)

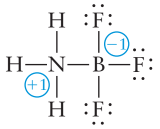


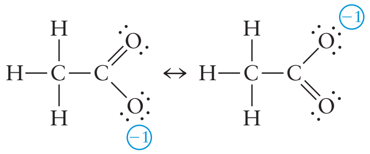
47.

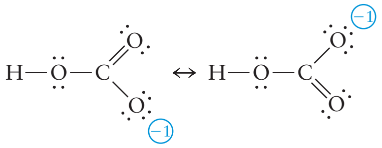


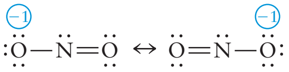
Bond lengths: N—H 1.01×10^{-10} m, N—C 1.47×10^{-10} m, C=O 1.20×10^{-10} m

49. 

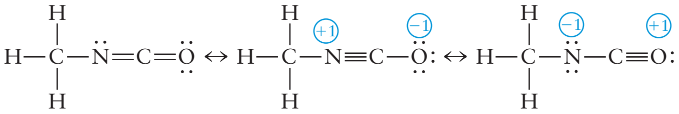
51. (a) 

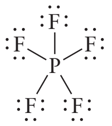
(b) 

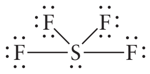
(c) 

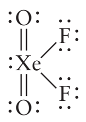
53. 

Between 1.18 × 10^{-10} m and 1.43 × 10^{-10} m.

55. 

57. (a) 

(b) 

(c) 

59. (a) SN = 4, tetrahedral (b) SN = 3, trigonal planar
(c) SN = 6, octahedral (d) SN = 4, pyramidal
(e) SN = 5, distorted T-shape

61. (a) SN = 6, square planar (b) SN = 4, bent, angle < 109.5°
(c) SN = 4, pyramidal, angle < 109.5° (d) SN = 2, linear

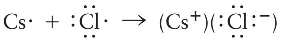
63. (a) SO_3 (b) NF_3 (c) NO_2^- (d) CO_3^{2-}

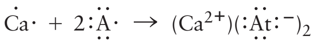
65. Only **(d)** and **(e)** are polar.

67. No, because VSEPR theory predicts a steric number of 3 and a bent molecule in both cases.

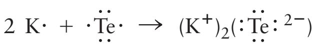
69. (a) Linear (b) The N end

71. $\overset{+2\,-1}{\text{SrBr}_2}$ $\overset{+2\,-2\,+1}{\text{Zn(OH)}_4^{2-}}$ $\overset{-4\,+1}{\text{SiH}_4}$ $\overset{+2\,+4\,-2}{\text{CaSiO}_3}$ $\overset{+6\,-2}{\text{Cr}_2\text{O}_7^{2-}}$ $\overset{+2\quad+5\,-2\quad-1}{\text{Ca}_5(\text{PO}_4)_3\text{F}}$ $\overset{+1\,-\frac{1}{2}}{\text{KO}_2}$ $\overset{+1\,-1}{\text{CsH}}$

73. (a) CsCl, cesium chloride 
$\text{Cs}\cdot + :\ddot{\underset{..}{\text{Cl}}}\cdot \rightarrow (\text{Cs}^+)(:\ddot{\underset{..}{\text{Cl}}}:^-)$

(b) CaAt_2, calcium astatide 
$\dot{\text{Ca}}\cdot + 2:\ddot{\underset{..}{\text{At}}}\cdot \rightarrow (\text{Ca}^{2+})(:\ddot{\underset{..}{\text{At}}}:^-)_2$

(c) Al_2S_3, aluminum sulfide 
$2\cdot\dot{\text{Al}}\cdot + 3\ \cdot\ddot{\underset{..}{\text{S}}}\cdot \rightarrow (\text{Al}^{3+})_2(:\ddot{\underset{..}{\text{S}}}:^{2-})_3$

(d) K_2Te, potassium telluride 
$2\ \text{K}\cdot + \cdot\ddot{\underset{..}{\text{Te}}}\cdot \rightarrow (\text{K}^+)_2(:\ddot{\underset{..}{\text{Te}}}:^{2-})$

75. (a) Aluminum oxide (b) Rubidium selenide
(c) Ammonium sulfide (d) Calcium nitrate
(e) Cesium sulfate (f) Potassium hydrogen carbonate

77. (a) AgCN (b) $Ca(OCl)_2$ (c) K_2CrO_4 (d) Ga_2O_3 (e) KO_2
(f) $Ba(HCO_3)_2$

79. Na_3PO_4, sodium phosphate

81. (a) SiO_2 (b) $(NH_4)_2CO_3$ (c) PbO_2 (d) P_2O_5 (e) CaI_2
(f) $Fe(NO_3)_3$

83. (a) Copper(I) sulfide and copper(II) sulfide (b) Sodium sulfate
(c) Tetraarsenic hexaoxide (d) Zirconium(IV) chloride
(e) Dichlorine heptaoxide (f) Gallium(I) oxide

CHAPTER 4

1. 0.66 m s^{-1}

3. 3.04 m

5. **(a)** 5.00×10^5 s^{-1} **(b)** 4.4 min

7. $\lambda = 1.313$ m; time = 0.0873 s

9. 2.7 K

11. Red

13. 550 nm, green

15. **(a)** 3.371×10^{-19} J **(b)** 203.0 kJ mol^{-1} **(c)** 4.926×10^{-3} mol s^{-1}

17. 5.895×10^{-7} m

19. $r_3 = 0.0952$ nm, $E_3 = -6.06 \times 10^{-18}$ J, energy per mole = 3.65×10^3 kJ mol^{-1}, $\nu = 1.14 \times 10^{16}$ s^{-1}, $\lambda = 2.63 \times 10^{-8}$ m = 26.3 nm

21. 72.90 nm, ultraviolet

23. Blue

25. Part of the yellow light, together with green and blue light, will eject electrons from cesium. No visible light will eject electrons from selenium; ultraviolet light is required.

27. **(a)** 7.4×10^{-20} J **(b)** 4.0×10^5 m s^{-1}

29. **(a)** 100 cm, 33 cm **(b)** two nodes

31. **(a)** 7.27×10^{-7} m **(b)** 3.96×10^{-10} m **(c)** 2.2×10^{-34} m

35. **(a)** 5.8×10^4 m s^{-1} **(b)** 7.9 m s^{-1}

37. $E_1 = 3.36 \times 10^{-18}$ J; $E_2 = 1.34 \times 10^{-17}$ J; $E_3 = 3.02 \times 10^{-17}$ J; $\lambda = 1.97 \times 10^{-8}$ m

39. **(a)** $\tilde{\Psi}_{21} = \tilde{\Psi}_{12}$ because the *x*- and *y*-axes are equivalent in a square box
(b) Exchanging *x* and *y* corresponds to a 90-degree rotation
(c) Exchanging labels cannot change the energy of the particle, a physically observable quantity

43. 1.6 Hz

45. 5.72×10^{-12} J = 0.357 eV

CHAPTER 5

1. Only **(b)** is allowed.

3. **(a)** 4*p* **(b)** 2*s* **(c)** 6*f*

5. **(a)** 2 radial, 1 angular **(b)** 1 radial, 0 angular **(c)** 2 radial, 3 angular

7. $R_{pz}^2 \propto \cos^2 q = 0$ for $q = p/2$; d_{xz} nodal planes are the *y*-*z* and *x*-*y* planes; $d_{x^2-y^2}$ nodal planes are two planes containing the *z*-axis at 45° from the *x*- and *y*-axes.

9. 3.17 Å, 2.64 Å

11. $\epsilon_{2s} = -0.396$ Ry $= -520$ kJ mol^{-1}

13. -1 Ry exactly, -0.396 Ry, -0.376 Ry

15. **(a)** $1s^22s^22p^2$ **(b)** [Ar]$3d^{10}4s^24p^4$ **(c)** [Ar]$3d^64s^2$

17. Be^+: $1s^22s^1$; C^-: $1s^22s^22p^3$; Ne^{2+}: $1s^22s^22p^4$; Mg^+: [Ne]$3s^1$; P^{2+}: [Ne]$3s^23p^1$; Cl^-: [Ne]$3s^23p^6$; As^+: [Ar]$3d^{10}4s^24p^2$; I^-: [Kr]$4d^{10}5s^25p^6$. All except Cl^- and I^- are paramagnetic.

19. **(a)** In **(b)** S^{2-} **(c)** Mn^{4+}

21. 117

23. First "noble gases" at $Z = 1, 5, 9$

25. 9.52 eV or 1.52×10^{-18} J

29. **(a)** $Z_{\text{eff},1s} = 7.12$ **(b)** $Z_{\text{eff},2s} = 0.79$ **(c)** $Z_{\text{eff},2p} = 0.47$

31. **(a)** K **(b)** Cs **(c)** Kr **(d)** K **(e)** Cl^-

33. **(a)** S^{2-} **(b)** Ti^{2+} **(c)** Mn^{2+} **(d)** Sr^{2+}

35. **(a)** For definition see Section 3.1. Helium has two electrons in the 1*s* orbital, which has the smallest radius. Moreover, each electron only partially screens the other from the nucleus, which has charge +2. Therefore, removal of the first electron requires considerable energy.
(b) Li, because Li^+ is essentially like He and explanation in **(a)** applies.
(c) 50.4 nm

37. **(a)** Start with Ca^{2+} and Ar, which are isoelectronic; that is, they have the same number of electrons. Ca^{2+} has the higher nuclear charge and is therefore smaller. Mg is above Ca in Group 2, so its 2+ ion is smaller than that of Ca. Br^- is larger than Cl^- in Group 7, which is, in turn, larger than Ar. Therefore, $Mg^{2+} < Ca^{2+} < Ar < Br^-$.
(b) Na has one *s* electron, well shielded from the nucleus; Ne and Na+ are isoelectronic, but Na+ has a net positive charge; O has an unfilled shell, but no special stability relative to Ne. Therefore, Na < O < Ne < Na+.
(c) Al is metallic, and thus electropositive; electronegativity sequence of others follows their relative horizontal positions in the periodic table. Therefore, Al < H < O < F.

39. 318.4 nm, near ultraviolet

CHAPTER 6

1. 0, 1, 2, 3, 2, 3 (6 σ orbitals in order of increasing energy)

5. The $1\sigma_g$ MO

7. Multiplying one of the two H atom orbitals by −1 is required for constructive interference; combination with two + signs leads to destruction interference.

9. H_2

11. He_2^+

15. Smaller bond energy; larger bond length

17. **(a)** F_2: $(\sigma_{g2s})^2(\sigma^*_{u2s})^2(\sigma_{g2p})^2(\pi_{u2p})^4(\pi^*_{g2p})^4$; F_2^+: $(\sigma_{g2s})^2(\sigma^*_{u2s})^2(\sigma_{g2p})^2(\pi_{u2p})^4(\pi^*_{g2p})^3$
(b) F_2: 1, F_2^+: $\frac{3}{2}$
(c) F_2^+ should be paramagnetic
(d) $F_2 < F_2^+$

19. $(\sigma_{g3s})^2(\sigma^*_{u3s})^2(\sigma_{g3pz})^2(\pi_{u3p})^4(\pi^*_{g3p})^2$; bond order = 2; paramagnetic

21. **(a)** F, 1 **(b)** N, $2\frac{1}{2}$ **(c)** O, $1\frac{1}{2}$

23. **(a)** is diamagnetic; **(b)** and **(c)** are paramagnetic

25. Bond order $2\frac{1}{2}$; paramagnetic

27. The outermost electron in CF is in a π^*_{2p} molecular orbital. Removing it gives a stronger bond.

29. $(\sigma_{1s})^2(\sigma^*_{1s})^2$; bond order = 0. It should be unstable.

31. Smaller because an antibonding electron is lost

33. Little change in dissociation energy or bond lengths because a nonbonding electron is lost

35. **(a)** IE = 15.6 eV, from $\sigma_{g_{2pz}}$, which is highest occupied level
(b) IE = 16.7 eV, from $\pi_{u_{2pxy}}$, which is second highest occupied level

39. 11.88 eV: the $4p_x$ or the $4p_y$ orbital; 15.2 eV: the σ orbital

41. Li_2: $\psi_\sigma^{\text{bond}}\,(1, 2; R_{AB}) = c_1[2s^A(1)2s^B(2) + 2s^A(2)2s^B(1)]$
C_2: $\psi_\pi^{\text{bond}}\,(1, 2, 3, 4; R_{AB} = c_1 R_{AB}[2p_y^A(1)\,2p_y^B(2)][2p_x^A(3)\,2p_x^B(4)] + c_1 R_A[2p_y^A(2)\,2p_y^B(1)]$
$[2p_x^A(4)\,2p_x^B(3)]$

43. Because the ground state of Be has no unpaired electrons, the simple VB model predicts that a bond will not form between two Be atoms. The same result is predicted by the LCAO approach. Two of the valence electrons in Be_2 occupy a bonding molecular orbital, but the other two must occupy an antibonding molecular orbital, leading to bond order zero.

45. $\psi_\sigma^{\text{bond}}(1, 2; R_{BH}) = C_1[1s^H(1)2p_z^B(2)] + C_2[1s^H(2)2p_z^B(1)]$
The simple VB model predicts a linear BO molecule. This is incorrect. The correct prediction is BH_3.

47. N has one unpaired electron in each of its $2p$ orbitals. Each of these can overlap with H $1s$ to form a σ bond whose wavefunction has the form

$\psi_\sigma = C_1[2p_a^N(1)1s^H(2)] + C_2[2p_a^N(2)1s^H(1)]$ where a is x, y, or z.

Because the $2p$ orbitals are mutally perpendicular, the simple VB model predicts a trigonal pyramid with angles of 90 degrees.

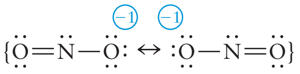
49. sp^3 hybridization of central N^-, bent molecular ion

51. (a) sp^3 on C, tetrahedral
(b) sp on C, linear
(c) sp^3 on O, bent
(d) sp^3 on C, pyramidal
(e) sp on Be, linear

53. sp^2 hybrid orbitals. ClO_3^+ is trigonal planar, ClO_2^+ is bent.

55. sp^3 hybrid orbitals, tetrahedral

59. Sixteen electrons, so molecule is linear; sp hybridization of central N gives two σ bonds, with $2p_z$ orbitals on outer nitrogen atoms (four electrons). Lone pairs on both $2s$ orbitals on outer nitrogen atoms (four atoms). π system as in Figure 16.21: $(\pi)^4(\pi^{nb})^4$ with eight electrons. Total bond order = 4; bond order 2 per N—N bond. N_3 and N_3^+ should be bound. N_3 and N_3^+ are paramagnetic.

61. 
$\{\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}=\overset{\cdot\cdot}{N}-\underset{\cdot\cdot}{\overset{(-1)}{\overset{\cdot\cdot}{O}}}: \leftrightarrow :\underset{\cdot\cdot}{\overset{(-1)}{\overset{\cdot\cdot}{O}}}-\overset{\cdot\cdot}{N}=\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\}$

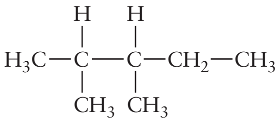
$SN = 3$, sp^2 hybridization, bent molecule. The $2p_z$ orbitals perpendicular to the plane of the molecule can be combined into a π molecular orbital containing one pair of electrons. This orbital adds bond order 1/2 to each N—O bond, for a total bond order of 3/2 per bond.

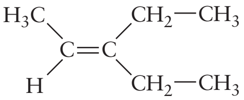
CHAPTER 7

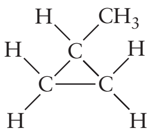
1. Yes, if the amount of knocking is less than that of iso-octane. Examples are the BTX compounds.

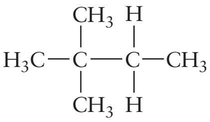
3. Ethane; $2\ C_2H_6(g) + 7\ O_2(g) \longrightarrow 4\ CO_2(g) + 6\ H_2O(\ell)$

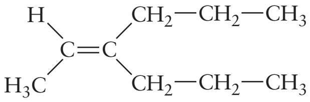
5. (a) $C_{10}H_{22} \longrightarrow C_5H_{10} + C_5H_{12}$
(b) Two: 1-pentene and 2-pentene

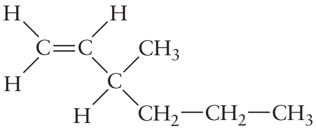
7. (a) 
$H_3C-\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle H}{|}}{C}}-\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle H}{|}}{C}}-CH_2-CH_3$

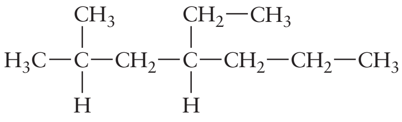
(b) 

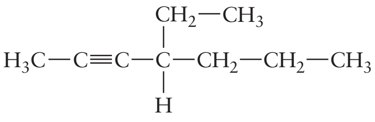
(c) 

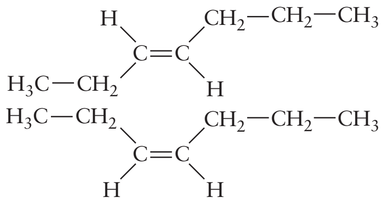
(d) 
$H_3C-\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}-\underset{\underset{\textstyle H}{|}}{\overset{\overset{\textstyle H}{|}}{C}}-CH_3$

(e) 

(f) 

(g) 
$H_3C-\underset{\underset{\textstyle H}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}-CH_2-\underset{\underset{\textstyle H}{|}}{\overset{\overset{\textstyle CH_2-CH_3}{|}}{C}}-CH_2-CH_2-CH_3$

(h) 
$H_3C-C\equiv C-\underset{\underset{\textstyle H}{|}}{\overset{\overset{\textstyle CH_2-CH_3}{|}}{C}}-CH_2-CH_2-CH_3$

9. 

11. (a) 1,2-Hexadiene
(b) 1,3,5-Hexatriene
(c) 2-Methyl-1-hexene
(d) 3-Hexyne

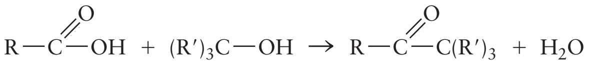
13. (a) sp^2, sp, sp^2, sp^3, sp^3, sp^3
(b) All sp^2
(c) sp^2, sp^2; all others sp^3
(d) sp^3, sp^3, sp, sp, sp^3, sp^3

15. 30 double bonds; on the bonds shared by two hexagonal faces

17. 11.2%; 4.49×10^9 kg

19. (a) $CH_3CH_2CH_2CH_2OH + CH_3COOH \longrightarrow CH_3COOCH_2CH_2CH_2CH_3 + H_2O$
(b) $NH_4CH_3COO \longrightarrow CH_3CONH_2 + H_2O$
(c) $CH_3CH_2CH_2OH \longrightarrow CH_3CH_2CHO$ (propionaldehyde) $+ H_2$
(d) $CH_3(CH_2)_5CH_3 + 11\ O_2 \longrightarrow 7\ CO_2 + 8\ H_2O$

21. (a) $CH_2{=}CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$; $CH_2BrCH_2Br \longrightarrow CH_2{=}CHBr + HBr$
(b) $CH_3CH_2CH{=}CH_2 + H_2O \longrightarrow CH_3CH_2CH(OH)CH_3$ (using H_2SO_4)
(c) $CH_3CH{=}CH_2 + H_2O \longrightarrow CH_3CH(OH)CH_3$ (using H_2SO_4);
$CH_3CH(OH)CH_3 \longrightarrow CH_3COCH_3 + H_2$ (copper or zinc oxide catalyst)

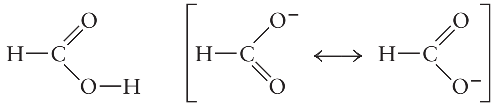
23. 

$$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH + (R')_3C{-}OH \rightarrow R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}C(R')_3 + H_2O$$

25. 79.9 L

27. $-CH_3$ carbon sp^3, other carbon sp^2. A π orbital with two electrons bonds the second carbon atom with the oxygen atom. The three groups around the second carbon form an approximately trigonal planar structure, with bond angles near 120 degrees. The geometry about the first carbon atom is approximately tetrahedral, with angles near 109.5 degrees.

29. The Lewis diagrams for HCOOH and $HCOO^-$ are



One resonance form is given for HCOOH, but two are given for the formate anion $HCOO^-$. In formic acid, one oxygen atom is doubly bonded to the carbon atom, and the other is singly bonded. In the anion, there is some double-bond character in both C—O bonds. The carbon atom in HCOOH is sp^2 hybridized (*SN* 3), and the OH oxygen atom is sp^3 hybridized (*SN* 4). The immediate surroundings of the carbon atom have trigonal planar geometry, and the C—O—H group is bent. In the $HCOO^-$, the carbon atom and both oxygen atoms are sp^2 hybridized (*SN* 3), possessing a three-center four-electron *p* system. In HCOOH, *p* overlap occurs between orbitals on the carbon atom and only one oxygen atom. Both the C— to —O bond lengths in the formate ion should lie somewhere between the value for the single bond (1.36 Å) and the value for the double bond (1.23 Å).

31. (a) Alcohol: $CH_3CH(OH)CH_3$, isopropyl alcohol; carboxylic acid:
$CH_3C(CH_3)(COCH_3)(CH_2)_3CH(CH_3)\ CH_2CH{=}CHC(CH_3){=}CHCOOH$
(b) 3,7,10-Trimethyl-2,4-dodecadiene

33. (a) $C_9H_8O_4$ (b) 1.80×10^{-3} mol

35. Dehydrogenate to make C=O bond from C—OH bond on first ring; move C=C bond from first to second ring; insert C=O group on third ring; remove hydrocarbon side chain on fourth ring together with hydrogen atom and replace it with an —OH group and a $-COCH_2OH$ group.

CHAPTER 8

1. (a) PtF_4 (b) PtF_6

3. $V_{10}O_{28}^{6-} + 16\ H_3O^+ \longrightarrow 10\ VO_2^+ + 24\ H_2O + 5$ state, V_2O_5

5. $2\ TiO_2 + H_2 \longrightarrow Ti_2O_3 + H_2O$ Titanium(III) oxide

7. Monodentate, at the N-atom lone pair

9. +2, +2, +2, 0

11. (a) $Na_2[Zn(OH)_4]$ (b) $[CoCl_2(en)_2]NO_3$
(c) $[Pt(H_2O)_3Br]Cl$ (d) $[Pt(NH_3)_4(NO_2)_2]Br_2$

13. (a) Ammonium diamminetetraisothiocyanatochromate(III)
(b) Pentacarbonyltechnetium(I) iodide
(c) Potassium pentacyanomanganate(IV)
(d) Tetra-ammineaquachlorocobalt(III) bromide

15. $[Cu(NH_3)_2Cl_2] < KNO_3 < Na_2[PtCl_6] < [Co(NH_3)_6]Cl_3$

21. (a) Strong: 1, weak: 5 (b) Strong or weak: 0
(c) Strong or weak: 3 (d) Strong: 2, weak: 4
(e) Strong: 0, weak: 4

23. $[Fe(CN)_6]^{3-}$: 1 unpaired, CFSE $= -2\ \Delta_o$; $[Fe(H_2O)_6]^{3+}$: 5 unpaired, CFSE $= 0$

25. d^3 gives half-filled and d^8 filled and half-filled shells for metal ions in an octahedral field. d^5 will be half filled and stable for high spin (small Δ_o), and d^6 will be a filled subshell and stable for low spin (large Δ_o).

27. This ion does not absorb any significant amount of light in the visible range.

29. $\lambda \approx 480$ nm; $\Delta_o \approx 250$ kJ mol^{-1}

31. -500 kJ mol^{-1}

33. (a) Orange–yellow
(b) Approximately 600 nm (actual: 575 nm)
(c) Decrease, because CN^- is a strong-field ligand and will increase Δ_o.

35. (a) Pale, because F^- is an even weaker field ligand than H_2O, so it should be high-spin d^5. This is a half-filled shell and the complex will absorb only weakly.
(b) Colorless, because Hg(II) is a d^{10} filled-subshell species

CHAPTER 9

1. $NH_4HS(s) \longrightarrow NH_3(g) + H_2S(g)$

3. $NH_4Br(s) + NaOH(aq) \longrightarrow NH_3(g) + H_2O(\ell) + NaBr(aq)$

5. 10.3 m

7. 1.40×10^4 ft

9. 1697.5 atm, 1.7200×10^3 bar

11. 0.857 atm

13. 8.00 L

15. 14.3 gill

17. 134 L

19. 35.2 psi

21. (a) 19.8 atm (b) 23.0 atm

23. The mass of a gas in a given volume changes proportionately to the absolute temperature. This statement will be true only at −19.8°C.

25. (a) $2\ Na(s) + 2\ HCl(g) \longrightarrow 2\ NaCl(s) + H_2(g)$ (b) 4.23 L

27. 3.0×10^6 L

29. 24.2 L

31. (a) 932 L H_2S (b) 1.33 kg, 466 L SO_2

33. $X_{SO_3} = 0.135$; $P_{SO_3} = 0.128$ atm

35. $X_{N_2} = 0.027$; $P_{N_2} = 1.6 \times 10^{-4}$ atm

37. **(a)** $X_{\text{CO}} = 0.444$ **(b)** $X_{\text{CO}} = 0.33$

39. **(a)** 5.8×10^{17} **(b)** 520 L

41. **(a)** 1.93×10^3 m s^{-1} = 1.93 km s^{-1} **(b)** 226 m s^{-1}

43. 6100 m s^{-1} (6000 K), 790 m s^{-1} (100 K)

45. Greater. As T increases, the Maxwell–Boltzmann distribution shifts to higher speeds.

47. $N_{\text{high}}/N_{\text{low}} = 0.91$

49. 5.3×10^{-4}

51. 2.42×10^{-9}

53. $P_h = 0.91$ atm

55. 162 atm = 2.38×10^3 psi

57. **(a)** 27.8 atm **(b)** 24.6 atm; attractive forces dominate.

59. 6.1×10^{-9} m

61. 92.6 g mol^{-1}

63. 1830 stages

65. 7.4×10^{-7} atm; 20 m^2 s^{-1}

CHAPTER 10

1. Gas

3. **(a)** Condensed **(b)** 10.3 cm^3 mol^{-1}

5. Condensed

7. The liquid water has vaporized to steam.

9. Harder, because forces binding the particles in NaCl are stronger and resist deformation better.

11. In all three phases, the diffusion constant should decrease as its density is increased. At higher densities, molecules are closer to each other. In gases, they will collide more often and travel shorter distances between collisions. In liquids and solids, there will be less space for molecules to move around each other.

13. Both involve the interaction of an ion with a dipole. In the first case, the dipole is permanent (preexisting), whereas in the second, it is induced by the approach of the ion. Induced dipole forces are weaker than ion–dipole forces. Examples: Na^+ with HCl (ion–dipole); Na^+ with Cl_2 (induced dipole).

15. **(a)** *Ion–ion,* dispersion **(b)** *Dipole–dipole,* dispersion
(c) *Dispersion* **(d)** *Dispersion*

17. Bromide ion

19. **(a)** 2.0×10^{-10} m; 2.5×10^{-10} m
(b) KCl has a longer bond yet lower potential energy (greater bond strength).

21. Heavier gases have stronger attractive forces, favoring the liquid and solid states.

23. Ne < NO < NH_3 < RbCl; nonpolar < polar < hydrogen-bonded < ionic

25. An eight-membered ring of alternating H and O atoms is reasonable. The ring is probably not planar.

27. The two have comparable molar masses, but the hydrogen-bonding in hydrazine should give it a higher boiling point.

29. 6.7×10^{25}

31. 6.16 L; several times smaller than the volume of 1 mol at standard temperature and pressure (22.4 L mol^{-1})

33. 7.02×10^{13} atoms cm^{-3}

35. 0.9345 g L^{-1}

37. 2.92 g $CaCO_3$

39. 0.69 atm; 31% lies below

41. Iridium. Its higher melting and boiling points indicate that the intermolecular forces in iridium are stronger than those in sodium.

43. No phase change will occur.

47. (a) Liquid (b) Gas (c) Solid (d) Gas

49. (a) Above. If gas and solid coexist at −84.0°C, their coexistence must extend upward in temperature to the triple point.
(b) The solid will sublime at some temperature below −84.0°C.

51. The meniscus between gas and liquid phases will disappear at the critical temperature, 126.19 K.

CHAPTER 11

1. (a) 5.53×10^{-3} M (b) 5.5×10^{-3} molal (c) 3.79 L

3. Molarity = 12.39 M in HCl; mole fraction of HCl = 0.2324; molality = 16.81 molal in HCl

5. 8.9665 molal

7. 0.00643 g H_2O

9. (a) 1.33 g mL^{-1} (b) 164 mL

11. 1.06 M in NaOH

13. (a) $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
(b) $K_2CO_3(s) + 2\ H^+(aq) \longrightarrow 2\ K^+(aq) + CO_2(g) + H_2O(\ell)$
(c) $2\ Cs(s) + 2\ H_2O(\ell) \longrightarrow 2\ Cs^+(aq) + 2\ OH^-(aq) + H_2(g)$
(d) $2\ MnO_4^-(aq) + 16\ H^+(aq) + 10\ Cl^-(aq) \longrightarrow 5\ Cl_2(g) + 2\ Mn^{2+}(aq) + 8\ H_2O(\ell)$

15. 16.8 mL of 7.91 M HNO_3

17. 6.74×10^3 L $CO_2(g)$

19. (a) $Ca(OH)_2(aq) + 2\ HF(aq) \longrightarrow CaF_2(aq) + 2\ H_2O(\ell)$
Hydrofluoric acid, calcium hydroxide, calcium fluoride
(b) $2\ RbOH(aq) + H_2SO_4(aq) \longrightarrow Rb_2SO_4(aq) + 2\ H_2O(\ell)$
Sulfuric acid, rubidium hydroxide, rubidium sulfate
(c) $Zn(OH)_2(s) + 2\ HNO_3(aq) \longrightarrow Zn(NO_3)_2(aq) + 2\ H_2O(\ell)$
Nitric acid, zinc hydroxide, zinc nitrate
(d) $KOH(aq) + CH_3COOH(aq) \longrightarrow KCH_3COO(aq) + H_2O(\ell)$
Acetic acid, potassium hydroxide, potassium acetate

21. Sodium sulfide

23. (a) $PF_3 + 3\ H_2O \longrightarrow H_3PO_3 + 3\ HF$
(b) $[H_3PO_3] = 0.0882$ M; $[HF] = 0.265$ M

25. 0.04841 M HNO_3

27. (a) $2\ \overset{+3}{P}F_2I(\ell) + 2\ \overset{0}{Hg}(\ell) \longrightarrow \overset{+2}{P}_2F_4(g) + \overset{+1}{Hg}_2I_2(s)$
(b) $2\ K\overset{+5}{Cl}\overset{-2}{O}_3(s) \longrightarrow 2\ K\overset{-1}{Cl}(s) + 3\ \overset{0}{O}_2(g)$
(c) $4\ \overset{-3}{N}H_3(g) + 5\ \overset{0}{O}_2(g) \longrightarrow 4\ \overset{+2}{N}\overset{-2}{O}(g) + 6\ H_2\overset{-2}{O}(g)$
(d) $2\ \overset{0}{As}(s) + 6\ Na\overset{+1}{O}H(\ell) \longrightarrow 2Na_3\overset{+3}{As}O_3(s) + 3\overset{0}{H}_2(g)$

29. $2\ \overset{0}{Au}(s) + 6\ H_2\overset{+6}{Se}O_4 \longrightarrow \overset{+3}{Au}_2(\overset{+6}{Se}O_4)_3(aq) + 3\ H_2\overset{+4}{Se}O_3(aq) + 3\ H_2O_6(\ell)$
Au is oxidized
Se is reduced (half of it)

31. (a) $2\ VO_2^+(aq) + SO_2(g) \longrightarrow 2\ VO^{2+}(aq) + SO_4^{2-}(aq)$
(b) $Br_2(\ell) + SO_2(g) + 6\ H_2O(\ell) \longrightarrow 2\ Br^-(aq) + SO_4^{2-}(aq) + 4\ H_3O^+(aq)$
(c) $Cr_2O_7^{2-}(aq) + 3\ Np^{4+}(aq) + 2\ H_3O^+(aq) \longrightarrow$
$2\ Cr^{3+}(aq) + 3\ NpO_2^{2+}(aq) + 3\ H_2O(\ell)$
(d) $5\ HCOOH(aq) + 2\ MnO_4^-(aq) + 6\ H_3O^+(aq) \longrightarrow$
$5\ CO_2(g) + 2\ Mn^{2+}(aq) + 14\ H_2O(\ell)$
(e) $3\ Hg_2HPO_4(s) + 2\ Au(s) + 8\ Cl^-(aq) + 3\ H_3O^+(aq) \longrightarrow$
$6\ Hg(\ell) + 3\ H_2PO_4^-(aq) + 2\ AuCl_4^-(aq) + 3\ H_2O(\ell)$

33. **(a)** $2\ \mathrm{Cr(OH)_3}(s) + 3\ \mathrm{Br_2}(aq) + 10\ \mathrm{OH^-}(aq) \longrightarrow 2\ \mathrm{CrO_4^{2-}}(aq) + 6\ \mathrm{Br^-}(aq) + 8\ \mathrm{H_2O}(\ell)$
(b) $\mathrm{ZrO(OH)_2}(s) + 2\ \mathrm{SO_3^{2-}}(aq) \longrightarrow \mathrm{Zr}(s) + 2\ \mathrm{SO_4^{2-}}(aq) + \mathrm{H_2O}(\ell)$
(c) $7\ \mathrm{HPbO_2^-}(aq) + 2\ \mathrm{Re}(s) \longrightarrow 7\ \mathrm{Pb}(s) + 2\ \mathrm{ReO_4^-}(aq) + \mathrm{H_2O}(\ell) + 5\ \mathrm{OH^-}(aq)$
(d) $4\ \mathrm{HXeO_4^-}(aq) + 8\ \mathrm{OH^-}(aq) \longrightarrow 3\ \mathrm{XeO_6^{4-}}(aq) + \mathrm{Xe}(g) + 6\ \mathrm{H_2O}(\ell)$
(e) $\mathrm{N_2H_4}(aq) + 2\ \mathrm{CO_3^{2-}}(aq) \longrightarrow \mathrm{N_2}(g) + 2\ \mathrm{CO}(g) + 4\ \mathrm{OH^-}(aq)$

35. **(a)** $\mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Fe^{3+}}(aq) + e^-$ oxidation
$\mathrm{H_2O_2}(aq) + 2\ \mathrm{H_3O^+}(aq) + 2\ e^- \longrightarrow 4\ \mathrm{H_2O}(\ell)$ reduction
(b) $5\ \mathrm{H_2O}(\ell) + \mathrm{SO_2}(aq) \longrightarrow \mathrm{HSO_4^-}(aq) + 3\ \mathrm{H_3O^+}(aq) + 2\ e^-$ oxidation
$\mathrm{Mn_4^-}(aq) + 8\ \mathrm{H_3O^+}(aq) + 5\ e^- \longrightarrow \mathrm{Mn^{2+}}(aq) + 12\ \mathrm{H_2O}(\ell)$ reduction
(c) $\mathrm{ClO_2^-}(aq) \longrightarrow \mathrm{ClO_2}(g) + e^-$ oxidation
$\mathrm{ClO_2^-}(aq) + 4\ \mathrm{H_3O^+}(aq) + 4\ e^- \longrightarrow \mathrm{Cl^-}(aq) + 6\ \mathrm{H_2O}(\ell)$ reduction

37. $3\ \mathrm{HNO_2}(aq) \longrightarrow \mathrm{NO_3^-}(aq) + 2\ \mathrm{NO}(g) + \mathrm{H_3O^+}(aq)$

39. 7.175×10^{-3} M $\mathrm{Fe^{2+}}(aq)$

41. 0.2985 atm

43. 3.34 K kg $\mathrm{mol^{-1}}$

45. 340 g $\mathrm{mol^{-1}}$

47. 1.7×10^2 g $\mathrm{mol^{-1}}$

49. −2.8°C. As the solution becomes more concentrated, its freezing point decreases further.

51. 2.70 particles (complete dissociation of $\mathrm{Na_2SO_4}$ gives 3 particles)

53. 1.88×10^4 g $\mathrm{mol^{-1}}$

55. 7.46×10^3 g $\mathrm{mol^{-1}}$

57. **(a)** 0.17 mol $\mathrm{CO_2}$
(b) Because the partial pressure of $\mathrm{CO_2}$ in the atmosphere is much less than 1 atm, the excess $\mathrm{CO_2}$ will bubble out from the solution and escape when the cap is removed.

59. 4.13×10^2 atm

61. 0.774

63. **(a)** 0.491 **(b)** 0.250 atm **(c)** 0.575

CHAPTER 12

1. -2.16×10^4 L atm $= -2.19 \times 10^6$ J

3. 86.6 m

5. 24.8, 28.3, 29.6, 31.0, and 32.2 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$, respectively; extrapolating gives about 33.5 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$ for Fr

7. 26.1, 25.4, 25.0, 24.3, 25.4, and 27.6 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$

9. **(a)** w is zero, q is positive, and ΔU is positive.
(b) w is zero, q is negative, and ΔU is negative.
(c) $(w_1 + w_2)$ is zero. $(\Delta U_1 + \Delta U_2) = (q_1 + q_2)$. The latter two sums could be any of three possibilities: both positive, both negative, or both zero.

11. 0.468 J $\mathrm{K^{-1}}$ $\mathrm{g^{-1}}$

13. $q_1 = Mc_{s_1}\Delta T_1 = -q_2 = -Mc_{s_2}\Delta T_2 \qquad \dfrac{C_{s_1}}{C_{s_2}} = \dfrac{\Delta T_2}{\Delta T_1}$

15. 314 J $\mathrm{g^{-1}}$ (modern value is 333 J $\mathrm{g^{-1}}$)

17. $w = -323$ J; $\Delta U = -393$ J; $q = -70$ J

19. **(a)** 38.3 L
(b) $w = -1.94 \times 10^3$ J; $q = 0$; $\Delta U = -1.94 \times 10^3$ J
(c) 272 K

21. $\Delta UE = +11.2$ kJ; $q = 0$; $w = +11.2$ kJ

23. **(a)** −6.68 kJ **(b)** +7.49 kJ **(c)** +0.594 kJ

25. 41.3 kJ

27. +513 J

29. 10.4°C

31. −623.5 kJ

33. A pound of diamonds. (This is recommended as a source of heat only as a last resort, however!)

35. −555.93 kJ

37. (a) −878.26 kJ (b) -1.35×10^7 kJ of heat absorbed

39. (a) −81.4 kJ (b) 55.1°C

41. $\Delta H_f^\circ = -152.3 \text{ kJ mol}^{-1}$

43. (a) $C_{10}H_8(s) + 12\ O_2(g) \longrightarrow 10\ CO_2(g) + 4\ H_2O(\ell)$
(b) −5157 kJ (c) −5162 kJ (d) $+84 \text{ kJ mol}^{-1}$

45. -264 kJ mol^{-1}

47. -1.58×10^3 kJ

49. Each side of the equation has three B—Br and three B—Cl bonds.

51. $w = -6.87$ kJ; $q = +6.87$ kJ; $\Delta U = \Delta H = 0$

53. $T_f = 144$ K; $w = \Delta U = -3.89$ kJ; $\Delta H = -6.48$ kJ

CHAPTER 13

1. (a) The system is all the matter participating in the reaction $NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq)$. This includes solid ammonium nitrate, the water in which it dissolves, and the aquated ions that are the products of the dissolution process. The surroundings include the flask or beaker in which the system is held, the air above the system, and other neighboring materials. The dissolution of ammonium nitrate is spontaneous after any physical separation (such as a glass wall or a space of air) between the water and the ammonium nitrate has been removed.

(b) The system is all the matter participating in the reaction $H_2(g) + O_2(g) \longrightarrow$ products. The surroundings are the walls of the bomb and other portions of its environment that might deliver heat or work or absorb heat or work. The reaction of hydrogen with oxygen is spontaneous. Once hydrogen and oxygen are mixed in a closed bomb, no constraint exists to prevent their reaction. It is found experimentally that this system gives products quite slowly at room temperature (no immediate explosion). It explodes instantly at higher temperatures.

(c) The system is the rubber band. The surroundings consist of the weight (visualized as attached to the lower end of the rubber band), a hanger at the top of the rubber band, and the air in contact with the rubber band. The change is spontaneous once a constraint such as a stand or support underneath the weight is removed.

(d) The system is the gas contained in the chamber. The surroundings are the walls of the chamber and the moveable piston head. The process is spontaneous if the force exerted by the weight on the piston exceeds the force exerted by the collisions of the molecules of the gas on the bottom of the piston. (The forces due to the mass of the piston itself and friction between the piston and the walls within which it moves are neglected.)

(e) The system is the drinking glass in the process glass ⟶ fragments. The surroundings are the floor, the air, and the other materials in the room. The change is spontaneous. It occurs when the constraint, which is whatever portion of the surroundings holds the glass above the floor, is removed.

3. (a) $6 \times 6 = 36$ (b) 1 in 36

5. The tendency for entropy to increase

7. $10^{-3.62 \times 10^{23}}$ (that is, 1 part in $10^{+3.62 \times 10^{23}}$)

9. (a) $\Delta S > 0$ (b) $\Delta S > 0$ (c) $\Delta S < 0$

11. (a) 0.333 (b) $q = -1000$ J (c) $w = -500$ J

13. $9.61 \text{ J K}^{-1} \text{ mol}^{-1}$

15. 29 kJ mol^{-1}

17. $\Delta U = \Delta H = 0$; $w = -1.22 \times 10^4$ J; $q = +1.22 \times 10^4$ J; $\Delta S = +30.5 \text{ J K}^{-1}$

19. $\Delta S_{\text{sys}} = +30.2\ \text{J K}^{-1}$; $\Delta S_{\text{surr}} = -30.2\ \text{J K}^{-1}$; $\Delta S_{\text{univ}} = 0$

21. $\Delta S_{\text{Fe}} = -8.24\ \text{J K}^{-1}$; $\Delta S_{\text{H}_2\text{O}} = +9.49\ \text{J K}^{-1}$; $\Delta S_{\text{tot}} = +1.25\ \text{J K}^{-1}$

23. **(a)** $-116.58\ \text{J K}^{-1}$ **(b)** Lower (more negative)

25. D$S^\circ = -162.54, -181.12, -186.14, -184.72, -191.08\ \text{J K}^{-1}$. The entropy changes in these reactions become increasingly negative with increasing atomic mass, except that the rubidium reaction is out of line.

27. ΔS_{surr} must be positive and greater in magnitude than $44.7\ \text{J K}^{-1}$.

29. $\Delta S_{\text{sys}} > 0$ because the gas produced (oxygen) has many possible microstates.

31. **(a)** $+740$ J **(b)** 2.65 kJ **(c)** No **(d)** 196 K

33. $q = +38.7$ kJ; $w = -2.92$ kJ; $\Delta U = +35.8$ kJ; $\Delta S_{\text{sys}} = +110\ \text{J K}^{-1}$; $\Delta G = 0$

35. Overall reaction: $2\ \text{Fe}_2\text{O}_3(s) + 3\ \text{C}(s) \longrightarrow 4\ \text{Fe}(s) + 3\ \text{CO}_2(g)$ $\Delta G = +840\ \text{J} + 3(-400)\ \text{J} = -360\ \text{J} < 0$

37. **(a)** $0 < T < 3000$ K
(b) $0 < K < 1050$ K
(c) Spontaneous at all temperatures

39. $\text{WO}_3(s) + 3\ \text{H}_2(g) \longrightarrow \text{W}(s) + 3\ \text{H}_2\text{O}(g)$
$\Delta H^\circ = 117.41$ kJ; $\Delta S^\circ = 131.19\ \text{J K}^{-1}$; $\Delta G < 0$ for $T > \Delta H^\circ/\Delta S^\circ = 895$ K

CHAPTER 14

1. **(a)** $\dfrac{P^2_{\text{H}_2\text{O}}}{P^2_{\text{H}_2}P_{\text{O}_2}} = K$ **(b)** $\dfrac{P_{\text{XeF}_6}}{P_{\text{Xe}}P^3_{\text{F}_2}} = K$ **(c)** $\dfrac{P^{12}_{\text{CO}_2}P^6_{\text{H}_2\text{O}}}{P^2_{\text{C}_6\text{H}_6}P^{15}_{\text{O}_2}} = K$

3. $P_4(g) + 6\ \text{Cl}_2(g) + 2\ \text{O}_2(g) \rightleftharpoons 4\ \text{POCl}_3(g)$ $\dfrac{P^4_{\text{POCl}_3}}{P_{\text{P}_4}P^6_{\text{Cl}_2}P^2_{\text{O}_2}} = K$

5. **(a)** $\dfrac{P_{\text{CO}_2}P_{\text{H}_2}}{P_{\text{CO}}P_{\text{H}_2\text{O}}} = K$ **(b)** 0.056 atm

7. **(a)** The graph is a straight line passing through the origin.
(b) The experimental K's range from 3.42×10^{-2} to 4.24×10^{-2}, with a mean of 3.84×10^{-2}.

9. **(a)** $\dfrac{(P_{\text{H}_2\text{S}})^8}{(P_{\text{H}_2})^8} = K$
(b) $\dfrac{(P_{\text{COCl}_2})(P_{\text{H}_2})}{(P_{\text{Cl}_2})} = K$
(c) $P_{\text{CO}_2} = K$
(d) $\dfrac{1}{(P_{\text{C}_2\text{H}_2})^3} = K$

11. **(a)** $\dfrac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = K$
(b) $\dfrac{[\text{VO}_3(\text{OH})^{2-}][\text{OH}^-]}{[\text{VO}_4^{3-}]} = K$
(c) $\dfrac{[\text{HCO}_3^-]^6}{[\text{As(OH)}_6^{3-}]^2P^6_{\text{CO}_2}} = K$

13. $\Delta G^\circ = -550.23$ kJ; $K = 2.5 \times 10^{96}$

15. **(a)** 2.6×10^{12} $\dfrac{P_{\text{SO}_3}}{(P_{\text{SO}_2})(P_{\text{O}_2})^{1/2}} = K$
(b) 5.4×10^{-35} $(P_{\text{O}_2})^{1/2} = K$
(c) 5.3×10^3 $[\text{Cu}^{2+}][\text{Cl}^-]^2 = K$

17. $K_1 = (K_2)^3$

19. K_2/K_1

21. 1.04×10^{-4}

23. 14.6

25. **(a)** $P_{SO_2} = P_{Cl_2} = 0.58$ atm; $P_{SO_2Cl_2} = 0.14$ atm **(b)** 2.4

27. **(a)** 0.180 atm **(b)** 0.756

29. $P_{PCl_5} = 0.078$ atm; $P_{PCl_3} = P_{Cl_2} = 0.409$ atm

31. $P_{Br_2} = 0.0116$ atm; $P_{I_2} = 0.0016$ atm; $P_{IBr} = 0.0768$ atm

33. $P_{N_2} = 0.52$ atm; $P_{O_2} = 0.70$ atm; $P_{NO} = 3.9 \times 10^{-16}$ atm

35. $P_{N_2} = 0.0148$ atm; $P_{H_2} = 0.0445$ atm; $P_{NH_3} = 0.941$ atm

37. 5.6×10^{-5} mol L^{-1}

39. 2.0×10^{-2}

41. **(a)** 0.31 atm **(b)** 1.65 atm, 0.15 atm

43. **(a)** 8.46×10^{-5} **(b)** 0.00336 atm

45. **(a)** 9.83×10^{-4} **(b)** Net consumption

47. $K > 5.1$

49. **(a)** $Q = 2.05$; reaction shifts to right.
(b) $Q = 3.27$; reaction shifts to left.

51. **(a)** 0.800, left
(b) $P_{P_4} = 5.12$ atm, $P_{P_2} = 1.77$ atm
(c) Dissociation

53. **(a)** Shifts left
(b) Shifts right
(c) Shifts right
(d) The volume must have been increased to keep the total pressure constant; shifts left
(e) No effect

55. **(a)** Exothermic **(b)** Decrease

57. Run the first step at low temperature and high pressure, and the second step at high temperature and low pressure.

59. Low temperature and high pressure

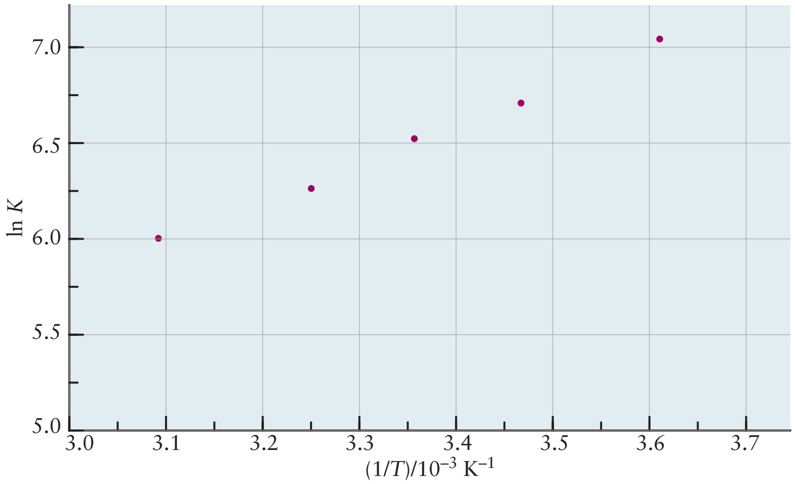
61. −58 kJ

63. **(a)** −56.9 kJ
(b) $\Delta H° = -55.6$ kJ, $\Delta S° = +4.2$ J K^{-1}

65. 4.3×10^{-3}

67. **(a)** 23.8 kJ mol^{-1}
(b) $T_b = 240$ K

69. **(a)**



(b) -16.8×10^3 J mol^{-1}

71. 76

73. **(a)** $K_1 = 1.64 \times 10^{-2}$; $K_2 = 5.4$ **(b)** 330

CHAPTER 15

1. **(a)** Cl^- cannot act as a Brønsted–Lowry acid.
(b) SO_4^{2-}
(c) NH_3
(d) NH_2^-
(e) OH^-

3. $HCO_3^-(aq)$ serves as the base.

5. **(a)** $CaO(s) + H_2O(\ell) \longrightarrow Ca(OH)_2(s)$
(b) The CaO acts as a Lewis base, donating a pair of electrons (located on the oxide ion) to one of the hydrogen ions (the Lewis acid) of the water molecule.

7. **(a)** Fluoride acceptor **(b)** Acids: BF_3, TiF_4; bases: ClF_3O_2, KF

9. **(a)** Base, $Mg(OH)_2$ **(b)** Acid, HOCl
(c) Acid, H_2SO_4 **(d)** Base, CsOH

11. $SnO(s) + 2\ HCl(aq) \longrightarrow Sn^{2+}(aq) + 2\ Cl^-(aq) + H_2O(\ell)$;
$SnO(s) + NaOH(aq) + H_2O(\ell) \longrightarrow Sn(OH)_3^-(aq) + Na^+(aq)$

13. 3.70

15. $3 \times 10^{-7}\ \text{M} < [H_3O^+] < 3 \times 10^{-6}\ \text{M}$; $3 \times 10^{-9}\ \text{M} < [OH^-] < 3 \times 10^{-8}\ \text{M}$

17. $[H_3O^+] = 1.0 \times 10^{-8}\ \text{M}$; $[OH^-] = 1.7 \times 10^{-6}\ \text{M}$

19. The first reaction is more likely to be correct. In the second case, the reactant H_3O^+ would be present at very low concentration (10^{-7} M) and would give neither a fast nor a vigorous reaction.

21. **(a)** $C_{10}H_{15}ON(aq) + H_2O(\ell) \rightleftharpoons C_{10}H_{15}ONH^+(aq) + OH^-(aq)$
(b) 7.1×10^{-11}
(c) Stronger

23. $K = 24$; $HClO_2$ is the stronger acid and NO_2^- the stronger base.

25. **(a)** Methyl orange **(b)** 3.8 to 4.4

27. 2.35

29. **(a)** 2.45 **(b)** 0.72 mol

31. 1.16

33. 1.2×10^{-6}

35. 10.4

37. 0.083 M

39. The reaction gives a base of moderate strength, the acetate ion, in solution, so the pH > 7.

41. $HCl < NH_4Br < KI < NaCH_3COO < NaOH$

43. 8.08

45. **(a)** 4.36 **(b)** 4.63

47. *m*-Chlorobenzoic acid

49. 639 mL

51. 13.88, 11.24, 7.00, 2.77

53. 2.86, 4.72, 8.71, 11.00

55. 11.89, 11.52, 10.79, 8.20, 6.05, 3.90, 1.95

57. 0.97 g

59. 0.0872 g, pH = 6.23 if no approximations are made, bromothymol blue

61. 4×10^{-7}

63. $[H_3AsO_4] = 8.0 \times 10^{-2}\ \text{M}$; $[H_2AsO_4^-] = [H_3O^+] = 2.0 \times 10^{-2}\ \text{M}$;
$[HAsO_4^{2-}] = 9.3 \times 10^{-8}\ \text{M}$; $[AsO_4^{3-}] = 1.4 \times 10^{-17}\ \text{M}$

65. $[PO_4^{3-}] = 0.020\ \text{M}$; $[HPO_4^{2-}] = [OH^-] = 0.030\ \text{M}$; $[H_2PO_4^-] = 1.61 \times 10^{-7}\ \text{M}$;
$[H_3PO_4] = 7.1 \times 10^{-18}\ \text{M}$

67. $[H_2CO_3] = 8.5 \times 10^{-6}$ M; $[HCO_3^-] = 1.5 \times 10^{-6}$ M; $[CO_3^{2-}] = 2.8 \times 10^{-11}$ M

69. 6.86

71. 1.51, 1.61, 2.07, 4.01, 6.07, 8.77, 9.29, 11.51

73. 46 kJ mol^{-1}

75. pK_{a1} should be smaller than 4.9; pK_{a2} should be larger.

77. Benzene

79. **(a)** CF_3COOH **(b)** $CH_3CH_2CHFCOOH$ **(c)** C_6H_5COOH

CHAPTER 16

1. 4.65 L

3. About 48°C

5. $Fe_2(SO_4)_3(s) \rightleftharpoons 2\ Fe^{3+}(aq) + 3\ SO_4^{2-}(aq)$ $[Fe^+]^2[SO_4^{2-}]^3 = K_{sp}$

7. 0.0665 g per 100 mL water

9. 14.3 g L^{-1}

11. $[I^-] = 6.2 \times 10^{-10}$ M, $[Hg_2^{2+}] = 3.1 \times 10^{-10}$ M

13. 1.9×10^{-12}

15. 1.6×10^{-8}

17. Yes. The initial reaction quotient is $6.2 \times 10^{-10} > K_{sp}$.

19. No

21. $[Pb^{2+}] = 2.3 \times 10^{-10}$ M; $[IO_3^-] = 0.033$ M

23. $[Ag^+] = 1.8 \times 10^{-2}$ M; $[CrO_4^{2-}] = 6.2 \times 10^{-9}$ M

25. 2.4×10^{-8} mol L^{-1}

27. **(a)** 3.4×10^{-6} M **(b)** 1.6×10^{-14} M

29. 9.1×10^{-3} M

31. In pure water: 1.2×10^{-4} M; at pH 7: 0.15 M

33. **(a)** Unchanged **(b)** Increase **(c)** Increase

35. **(a)** 8.6×10^{-4} M, Pb^{2+} in solid **(b)** 3.1×10^{-7}

37. $[I^-] = 5.3 \times 10^{-4}$ M

39. 2×10^{-13} M

41. pH = 2.4; $[Pb^{2+}] = 6 \times 10^{-11}$ M

43. $[Cu(NH_3)_4^{2+}] = 0.10$ M; $[Cu^{2+}] = 7 \times 10^{-14}$ M

45. $[K^+] = 0.0051$ M and $[Na^+] = 0.0076$ M

47. More will dissolve in 1 M NaCl (3×10^{-5} versus 1.3×10^{-5} mol L^{-1}). Less will dissolve in 0.100 M NaCl (3×10^{-6} versus 1.3×10^{-5} mol L^{-1}).

49. $Cu^{2+}(aq) + 2\ H_2O(\ell) \rightleftharpoons CuOH^+(aq) + H_3O^+(aq)$ or
$Cu(H_2O)_4^{2+}(aq) + H_2O(\ell) \rightleftharpoons Cu(H_2O)_3OH^+(aq) + H_3O^+(aq)$

51. 5.3

53. $K_a = 9.6 \times 10^{-10}$

55. In the first case, solid $Pb(OH)_2$ will precipitate; $[Pb^{2+}] = 4.2 \times 10^{-13}$ M, $[Pb(OH)_3^-] =$ 0.17 M. In the second case, solid $Pb(OH)_2$ will not precipitate; $[Pb^{2+}] = 1 \times 10^{-13}$ M, $[Pb(OH)_3^-] = 0.050$ M.

CHAPTER 17

3. 0.180 mol

5. **(a)** $Zn(s) + Cl_2(g) \longrightarrow Zn^{2+}(aq) + 2\ Cl^-(aq)$
(b) 1.20×10^3 C; 1.24×10^{-2} mol e^-
(c) Decreases by 0.407 g **(d)** 0.152 L Cl_2 consumed

7. +2

9. **(a)** Anode: $Cl^- \longrightarrow \frac{1}{2}Cl_2(g) + e^-$; cathode: $K^+ + e^- \longrightarrow K(\ell)$
total: $Cl^- + K^+ \longrightarrow K(\ell) + \frac{1}{2}Cl_2(g)$
(b) Mass K = 14.6 g; mass Cl_2 = 13.2 g

11. $\Delta G° = -921$ J; $w_{max} = +921$ J

13. **(a)** Anode: $Co \longrightarrow Co^{2+} + 2\,e^-$; cathode: $Br_2 + 2\,e^- \longrightarrow 2\,Br^-$;
total: $Co + Br_2 \longrightarrow Co^{2+} + 2\,Br^-$
(b) 1.34 V

15. **(a)** Anode: $Zn \longrightarrow Zn^{2+} + 2\,e^-$; cathode: $In^{3+} + 3\,e^- \longrightarrow In$
(b) -0.338 V

17. Reducing agent

19. Br_2 less effective than Cl_2

21. **(a)** BrO_3^- **(b)** Cr **(c)** Co

23. **(a)** $\mathscr{E}° = -0.183$ V **(b)** It will not disproportionate.

25. **(a)** No **(b)** Br^-

27. 0.37 V

29. -0.31 V

31. 5.17

33. **(a)** 0.31 V **(b)** 1×10^{-8} M

35. $K = 3 \times 10^{31}$, orange

37. 3×10^6

39. pH = 2.53; $K_a = 0.0029$

41. **(a)** 1.065 V **(b)** 1.3×10^{-11} M **(c)** 7.6×10^{-13}

43. 2.041 V; 12.25 V

45. **(a)** 9.3×10^6 C **(b)** 1.1×10^8 J

47. No, because $H_2SO_4(aq)$ is not the only substance whose amount changes during discharge. The accumulated $PbSO_4$ must also be removed and replaced by Pb and PbO_2.

49. 7900 J g^{-1}

51. $\Delta\mathscr{E}° = -0.419$ V, not spontaneous under standard conditions (pH = 14). If $[OH^-]$ is small enough, the equilibrium will shift to the right and the reaction will become spontaneous.

53. According to its reduction potential, yes. In practice, however, the sodium would react instantly and explosively with the water and would therefore be useless for this purpose.

55. $2\,Cl^- \longrightarrow Cl_2(g) + 2\,e^-$ anode
$Na^+ + e^- \longrightarrow Na(\ell)$ cathode

57. 4.4×10^4 kg

59. $2\,Mg + TiCl_4 \longrightarrow Ti + 2\,MgCl_2$; 102 kg

61. 42.4 min

63. **(a)** Ni
(b) 21.9 g (provided the electrolyte volume is very large)
(c) H_2

CHAPTER 18

1. 5.3×10^{-5} mol L^{-1} s^{-1}

3. $$\text{rate} = -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

5. **(a)** Rate = $k[NO]^2[H_2]$; k has the units L^2 mol^{-2} s^{-1}
(b) An increase by a factor of 18

7. **(a)** Rate = $k[C_5H_5N][CH_3I]$ **(b)** $k = 75$ L mol^{-1} s^{-1}
(c) 7.5×10^{-8} mol L^{-1} s^{-1}

9. 3.2×10^{4} s

11. 0.0019 atm

13. $5.3 \times 10^{-3}\ \text{s}^{-1}$

15. 2.34×10^{-5} M

17. 2.9×10^{-6} s

19. (a) Bimolecular, rate = $k[\text{HCO}][\text{O}_2]$
(b) Termolecular, rate = $k[\text{CH}_3][\text{O}_2][\text{N}_2]$
(c) Unimolecular, rate = $k[\text{HO}_2\text{NO}_2]$

21. (a) The first step is unimolecular; the others are bimolecular.
(b) $\text{H}_2\text{O}_2 + \text{O}_3 \longrightarrow \text{H}_2\text{O} + 2\ \text{O}_2$
(c) O, ClO, CF_2Cl, Cl

23. $0.26\ \text{L mol}^{-1}\ \text{s}^{-1}$

25. (a) $\text{A} + \text{B} + \text{E} \longrightarrow \text{D} + \text{F}$ $\qquad \text{rate} = \dfrac{k_1 k_2}{k_{-1}} \dfrac{[\text{A}][\text{B}][\text{E}]}{[\text{D}]}$

(b) $\text{A} + \text{D} \longrightarrow \text{B} + \text{F}$ $\qquad \text{rate} = \dfrac{k_1 k_2 k_3}{k_{-1} k_{-2}} \dfrac{[\text{A}][\text{D}]}{[\text{B}]}$

27. Only mechanism (b)

29. Only mechanism (a)

31. $\text{rate} = \dfrac{k_2 k_1 [\text{A}][\text{B}][\text{E}]}{k_2[\text{E}] + k_{-1}[\text{D}]}$ $\qquad$ When $k_2[\text{E}] \ll k_{-1}[\text{D}]$

33. $\dfrac{d[\text{Cl}_2]}{dt} = \dfrac{k_1 k_2 [\text{NO}_2\text{Cl}]^2}{k_{-1}[\text{NO}_2] + k_2[\text{NO}_2\text{Cl}]}$

35. (a) 4.25×10^{5} J $\qquad$ (b) $1.54 \times 10^{11}\ \text{L mol}^{-1}\ \text{s}^{-1}$

37. (a) $1.49 \times 10^{-3}\ \text{L mol}^{-1}\ \text{s}^{-1}$ $\qquad$ (b) 1.30×10^{3} s

39. (a) $4.3 \times 10^{13}\ \text{s}^{-1}$ $\qquad$ (b) $1.7 \times 10^{5}\ \text{s}^{-1}$

41. $70.3\ \text{kJ mol}^{-1}$

43. $6.0 \times 10^{9}\ \text{L mol}^{-1}\ \text{s}^{-1}$

45. (a) $1.2 \times 10^{-3}\ \text{mol L}^{-1}\ \text{s}^{-1}$ $\qquad$ (b) 5×10^{-5} M

CHAPTER 19

1. (a) $2\ {}^{12}_{6}\text{C} \longrightarrow {}^{23}_{12}\text{Mg} + {}^{1}_{0}n$
(b) ${}^{15}_{7}\text{N} + {}^{1}_{1}\text{H} \longrightarrow {}^{12}_{6}\text{C} + {}^{4}_{2}\text{He}$
(c) $2\ {}^{3}_{2}\text{He} \longrightarrow {}^{4}_{2}\text{He} + 2\ {}^{1}_{1}\text{H}$

3. (a) $3.300 \times 10^{10}\ \text{kJ mol}^{-1}$ = 342.1 MeV total; 8.551 MeV per nucleon
(b) $7.312 \times 10^{10}\ \text{kJ mol}^{-1}$ = 757.9 MeV total; 8.711 MeV per nucleon
(c) $1.738 \times 10^{11}\ \text{kJ mol}^{-1}$ = 1801.7 MeV total; 7.570 MeV per nucleon

5. The two ${}^{4}\text{He}$ atoms are more stable, with a mass lower than that of one ${}^{8}\text{Be}$ atom by 9.86×10^{-5} u.

7. 16.96 MeV

9. (a) ${}^{39}_{17}\text{Cl} \longrightarrow {}^{39}_{18}\text{Ar} + {}^{0}_{-1}e^{-} + \tilde{\nu}$
(b) ${}^{22}_{11}\text{Na} \longrightarrow {}^{22}_{10}\text{Ne} + {}^{0}_{-1}e^{+} + \nu$
(c) ${}^{224}_{88}\text{Ra} \longrightarrow {}^{220}_{86}\text{Rn} + {}^{4}_{2}\text{He}$
(d) ${}^{82}_{38}\text{Sr} + {}^{0}_{-1}e^{-} \longrightarrow {}^{82}_{37}\text{Rb} + \nu$

11. ${}^{19}\text{Ne}$ decays to ${}^{19}\text{F}$ by positron emission; ${}^{23}\text{Ne}$ decays to ${}^{23}\text{Na}$ by beta decay.

13. An electron, 0.78 MeV

15. ${}^{30}_{14}\text{Si} + {}^{1}_{0}n \longrightarrow {}^{31}_{14}\text{Si} \longrightarrow {}^{31}_{15}\text{P} + {}^{0}_{-1}e^{-} + \tilde{\nu}$

17. ${}^{210}_{84}\text{Po} \longrightarrow {}^{206}_{82}\text{Pb} + {}^{4}_{2}\text{He}$ $\qquad {}^{4}_{2}\text{He} + {}^{9}_{4}\text{Be} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}n$

19. $3.7 \times 10^{10}\ \text{min}^{-1}$

21. (a) 1.0×10^{6} $\qquad$ (b) 5.9×10^{4}

23. 1.6×10^{18} disintegrations s^{-1}

25. 4200 years

27. 3.0×10^9 years

29. 6.0×10^9 years

31. ${}^{11}_{6}\text{C} \longrightarrow {}^{11}_{5}\text{B} + {}^{0}_{1}e^{+} + n$; ${}^{15}_{8}\text{O} \longrightarrow {}^{15}_{7}\text{N} + {}^{0}_{1}e^{+} + n$

33. Exposure from ${}^{15}\text{O}$ is greater by a factor of $1.72/0.99 = 1.74$.

35. **(a)** 2.3×10^{10} Bq
(b) 0.024 mGy
(c) Yes. A dose of 5 Gy has a 50% chance of being lethal; this dose is greater than 8.5 Gy in the first 8 days.

37. **(a)** ${}^{90}_{38}\text{Sr} \longrightarrow {}^{90}_{40}\text{Zr} + 2\,{}^{0}_{-1}e^{-} + 2\tilde{\nu}$
(b) 2.8 MeV
(c) 5.23×10^{12} disintegrations s^{-1}
(d) 4.44×10^{11} disintegrations s^{-1}

39. Increase (assuming no light isotopes of U are products of the decay)

41. 7.59×10^7 kJ g^{-1}

CHAPTER 20

1. **(a)** $A = 0.699$ **(b)** $\epsilon = 1.4 \times 10^3$ L mol^{-1} cm^{-1}

3. $c_A = 0.000368$ mol L^{-1}
$c_B = 0.00157$ mol L^{-1}

5. 6.736×10^{-23} J = 40.56 J mol^{-1}

7. **(a)** 1.45×10^{-46} kg m^2
(b) $E_1 = 7.65 \times 10^{-23}$ J; $E_2 = 2.30 \times 10^{-22}$ J; $E_3 = 4.59 \times 10^{-22}$ J
(c) 1.13 Å

9. **(a)** 5.12 **(b)** 6.80×10^{-2} **(c)** 3.23×10^{-6}

11. 25.4 kg s^{-2}

13. 5.1×10^2 kg s^{-2}

15. 5.3×10^{-4}

17. Decrease, because the electron will enter a π^* antibonding orbital

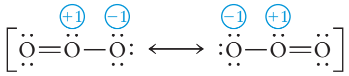
19. In the blue range, around 450 nm

21. Shorter; the π bonding is localized in cyclohexene.

23. 474 nm

25. 2, 3 : 2; 1; 2, 6 : 1

27. 2.72×10^{-7} m

29. 

$SN = 3$, sp^2 hybridization, bent molecule
Two electrons in a π orbital formed from the three $2p_z$ orbitals perpendicular to the molecular plane, total bond order of $\frac{3}{2}$ for each O—O bond.

31. 8 molecules

CHAPTER 21

1. **(b)**, **(c)**, and **(d)**

3. Two mirror planes, one 2-fold rotation axis

5. 3.613 Å

7. 102.9°

9. 49.87° and 115.0°

11. **(a)** 5.675×10^6 Å^3 **(b)** 5×10^{14}

13. 4.059 g cm^{-3}

15. **(a)** 1.602×10^{-22} cm^3 **(b)** 3.729×10^{-22} g
(c) 4.662×10^{-23} g **(d)** 6.025×10^{23} (in error by 0.05%)

17. 8

19. ReO_3

21. (a) 2.48 Å (b) 2.87 Å (c) 1.24 Å

23. (a) 2 (b) 0.680

25. 0.732

27. (a) Ionic (b) Covalent (c) Molecular (d) Metallic

29. $CO < BaCl_2 < Co < SiC$

33. 8, 6, 12

35. 664 kJ mol^{-1}

37. (a) 1041 kJ mol^{-1} (b) 1205 kJ mol^{-1}

39. Not by a significant amount because each vacancy is accompanied by an interstitial. In large numbers, such defects could cause a small bulging of the crystal and a decrease in its density.

41. (a) $Fe_{0.9352}O$ (b) 13.86% of the iron

CHAPTER 22

1. The structures of $P_2O_7^{4-}$ and $S_2O_7^{2-}$ have the same number of electrons and are found by writing "P" or "S" in place of "Si" and adjusting the formal charges. The chlorine compound is Cl_2O_7, dichlorine heptaoxide.

3. (a) Tetrahedra; Ca: +2, Fe: +3, Si: +4, O: −2
(b) Infinite sheets; Na: +1, Zr: +2, Si: +4, O: −2
(c) Pairs of tetrahedra; Ca: +2, Zn: +2, Si: +4, O: −2
(d) Infinite sheets; Mg: +2, Si: +4, O: −2, H: +1

5. (a) Infinite network; Li: +1, Al: +3, Si: +4, O: −2
(b) Infinite sheets; K: +1, Al: +3, Si: +4, O: −2, H: +1
(c) Closed rings or infinite single chains; Al: +3, Mg: +2, Si: +4, O: −2

7. $Mg_3Si_4O_{10}(OH)_2(s) \longrightarrow 3\ MgSiO_3(s) + SiO_2(s) + H_2O(g)$

9. 234 L

11. 0.418 mol Si, 0.203 mol Na, 0.050 mol Ca, 0.0068 mol Al, 0.002 mol Mg, 0.0005 mol Ba

13. −113.0 kJ

15. $\frac{7}{3}$

17. (a) $SiO_2(s) + 3\ C(s) \longrightarrow SiC(s) + 2\ CO(g)$
(b) +624.6 kJ mol^{-1}
(c) Low conductivity, high melting point, very hard

19. −1188.2 kJ, unstable

21. 24 $(\Omega\ m)^{-1}$ or 24 S m^{-1}

23. 1.26 C $V^{-1}\ s^{-1}\ m^{-1}$ or 1.26 $(\Omega\ m)^{-1}$ or 1.26 S m^{-1}

25. 1.48 electrons per Cu atom

27. 2.16×10^{-19} J

29. 6.1×10^{-27} electrons; that is, no electrons

31. (a) Electron movement (*n*-type)
(b) Hole movement (*p*-type)

33. 680 nm, red

35. Decrease

CHAPTER 23

1. $n\ CCl_2{=}CH_2 \longrightarrow -(CCl_2-CH_2-)_n$

3. Formaldehyde, $CH_2{=}O$

5. (a) H_2O (b) $-(NH-CH_2-CO-)$

7. 646 kg adipic acid and 513 kg hexamethylenediamine

9. 3.49×10^{12} L = 3.49×10^{9} m^3 = 3.49 km^3

11. The isotropic phase has higher entropy and higher enthalpy.

13. A micelle (containing hydrocarbon in the interior and water on the outside)

15. 5 chiral centers

17. 27

19. In octane, because the side groups are all hydrocarbon

21. C_9H_9NO; 119 units

APPENDIX A

1. (a) 5.82×10^{-5} (b) 1.402×10^{3} (c) 7.93
(d) -6.59300×10^{3} (e) 2.530×10^{-3} (f) 1.47

3. (a) 0.000537 (b) 9,390,000 (c) −0.00247
(d) 0.00620 (e) 20,000

5. 746,000,000 kg

7. (a) The value is 135.6 (b) 111.34 g (c) 0.22 g, 0.23 g

9. That of the mass in problem 7

11. (a) 5 (b) 3 (c) Either two or three (d) 3 (e) 4

13. (a) 14 L (b) −0.0034°C (c) 340 lb = 3.4×10^{2} lb
(d) 3.4×10^{2} miles (e) 6.2×10^{-27} J

15. 2,997,215.55

17. (a) −167.25 (b) 76 (c) 3.1693×10^{15} (d) -7.59×10^{-25}

19. (a) −8.40 (b) 0.147 (c) 3.24×10^{-12} (d) 4.5×10^{13}

21. $A = 337$ cm^2

APPENDIX B

1. (a) 6.52×10^{-11} kg (b) 8.8×100^{-11} s (c) 5.4×10^{12} kg m^2 s^{-3}
(d) 1.7×10^{4} kg m^2 s^{-3} A^{-1}

3. (a) 4983°C (b) 37.0°C (c) 111°C (d) −40°C

5. (a) 5256 K (b) 310.2 K (c) 384 K (d) 233 K

7. (a) 24.6 m s^{-1} (b) 1.51 × 103 kg m^{-3} (c) 1.6×10^{-29} A s m
(d) 1.5×10^{2} mol m^{-3} (e) 6.7 kg m^2 s^{-3} = 6.7 W

9. 1 kW-hr = 3.6×10^{6} J; 15.3 kW-hr = 5.51×10^{7} J

11. 6620 cm^3 or 6.62 L

13. 3×10^{2} J

15. (a) 55 J
(b) O (No work was done because no displacement was achieved.)

APPENDIX C

1. 50 miles per hour

3. (a) Slope = 4, intercept = −7

(b) Slope = $\frac{7}{2} = 3.5$, intercept = $-\frac{5}{2} = -2.5$

(c) Slope = −2, intercept = $\frac{4}{3} = 1.3333\ldots$

5. The graph is not a straight line.

7. (a) $-\frac{5}{7} = -0.7142857\ldots$ (b) $\frac{3}{4} = 0.75$ (c) $\frac{2}{3} = 0.6666\ldots$

9. (a) 0.5447 and −2.295 (b) −0.6340 and −2.366 (c) 2.366 and 0.6340

11. (a) 6.5×10^{-7} (also two complex roots)
(b) 4.07×10^{-2} (also 0.399 and −1.011)
(c) −1.3732 (also two complex roots)

13. (a) 4.551 (b) 1.53×10^{-7} (c) 2.6×10^{8} (d) -48.7264

15. 3.015

17. 121.477

19. 7.751 and -2.249

21. $x = 1.086$

23. (a) $8x$ (b) $3 \cos 3x - 8 \sin 2x$ (c) 3 (d) $\frac{1}{x}$

25. (a) 20 (b) $\frac{78125}{7}$ (c) 0.0675

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Index/Glossary

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Locations of Some Important Tables of Data

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Ionization Constants K_a of Acids at 25°C	page 634
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Reduction Potentials at 25°C	page A.45
Solubility Product Constants K_{sp} at 25°C	page 682
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Wave Functions for One-Electron Atoms	page 175

Relative Atomic Masses of the Elements

The atomic masses of many elements are not invariant but depend on the origin and treatment of the material. The values given here apply to elements as they exist naturally on earth. Values in parentheses are used for radioactive elements whose atomic masses cannot be quoted precisely without knowledge of the origins of the elements; the value given is the relative atomic mass of the isotope of that element having the longest half-life. Elements 112, 113, 114, 115, 116, and 118 have not yet been granted official status by the International Union of Pure and Applied Chemistry (IUPAC). In these six cases, either only preliminary or no good mass spectroscopy data exist, so the numbers in parentheses contain either only the latest available mass number or the mass number of the main isotope that was studied.

Name	Symbol	Atomic Number	Relative Atomic Mass
Actinium	Ac	89	(227.0278)
Aluminum	Al	13	26.9815386
Americium	Am	95	(243.0614)
Antimony	Sb	51	121.760
Argon	Ar	18	39.948
Arsenic	As	33	74.92160
Astatine	At	85	(209.9871)
Barium	Ba	56	137.327
Berkelium	Bk	97	(247.0703)
Beryllium	Be	4	9.012182
Bismuth	Bi	83	208.98040
Bohrium	Bh	107	(272.1380)
Boron	B	5	10.811
Bromine	Br	35	79.904
Cadmium	Cd	48	112.411
Calcium	Ca	20	40.078
Californium	Cf	98	(251.0796)
Carbon	C	6	12.0107
Cerium	Ce	58	140.116
Cesium	Cs	55	132.9054519
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.9961
Cobalt	Co	27	58.933195
Copper	Cu	29	63.546
Curium	Cm	96	(247.0704)
Darmstadtium	Ds	110	(281.162)
Dubnium	Db	105	(268.1255)
Dysprosium	Dy	66	162.500
Einsteinium	Es	99	(252.0830)
Erbium	Er	68	167.259
Europium	Eu	63	151.964
Fermium	Fm	100	(257.0951)
Fluorine	F	9	18.9984032
Francium	Fr	87	(223.0197)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.723
Germanium	Ge	32	72.64
Gold	Au	79	196.966569
Hafnium	Hf	72	178.49
Hassium	Hs	108	(277.150)
Helium	He	2	4.002602
Holmium	Ho	67	164.93032
Hydrogen	H	1	1.00794
Indium	In	49	114.818
Iodine	I	53	126.90447
Iridium	Ir	77	192.217
Iron	Fe	26	55.845
Krypton	Kr	36	83.798
Lanthanum	La	57	138.90547
Lawrencium	Lr	103	(262.1096)
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	174.967
Magnesium	Mg	12	24.3050
Manganese	Mn	25	54.938045
Meitnerium	Mt	109	(276.1512)
Mendelevium	Md	101	(258.0984)
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.242
Neon	Ne	10	20.1797
Neptunium	Np	93	(237.0482)
Nickel	Ni	28	58.6934
Niobium	Nb	41	92.90638
Nitrogen	N	7	14.00674
Nobelium	No	102	(259.1010)
Osmium	Os	76	190.23
Oxygen	O	8	15.9994
Palladium	Pd	46	106.42
Phosphorus	P	15	30.973762
Platinum	Pt	78	195.084
Plutonium	Pu	94	(244.0642)
Polonium	Po	84	(208.9824)
Potassium	K	19	39.0983
Praseodymium	Pr	59	140.90765
Promethium	Pm	61	(144.9127)
Protactinium	Pa	91	231.03588
Radium	Ra	88	(226.0254)
Radon	Rn	86	(222.0176)
Rhenium	Re	75	186.207
Rhodium	Rh	45	102.90550
Roentgenium	Rg	111	(280.1645)
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(267.1215)
Samarium	Sm	62	150.36
Scandium	Sc	21	44.955912
Seaborgium	Sg	106	(271.1335)
Selenium	Se	34	78.96
Silicon	Si	14	28.0855
Silver	Ag	47	107.8682
Sodium	Na	11	22.98976928
Strontium	Sr	38	87.62
Sulfur	S	16	32.065
Tantalum	Ta	73	180.94788
Technetium	Tc	43	(97.9064)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92535
Thallium	Tl	81	204.3833
Thorium	Th	90	232.03806
Thulium	Tm	69	168.93421
Tin	Sn	50	118.710
Titanium	Ti	22	47.867
Tungsten	W	74	183.84
Ununbium	Uub	112	(285)
Ununhexium	Uuh	116	(293)
Ununoctium	Uuo	118	(294)
Ununpentium	Uup	115	(288.192)
Ununquadium	Uuq	114	(289.189)
Ununtrium	Uut	113	(285.174)
Uranium	U	92	238.02891
Vanadium	V	23	50.9415
Xenon	Xe	54	131.293
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.90585
Zinc	Zn	30	65.409
Zirconium	Zr	40	91.224

Source: Commission on Atomic Weights and Isotopic Abundances, International Union of Pure and Applied Chemistry, *Pure and Applied Chemistry,* Vol. 78, 2051–2066 (2006).