



Under atmospheric conditions, solid carbon dioxide (dry ice) does not melt; it only sublimes.

## Intermolecular Forces and Liquids and Solids

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### ESSENTIAL CONCEPTS

**Intermolecular Forces** Intermolecular forces, which are responsible for the nonideal behavior of gases, also account for the existence of the condensed states of matter—liquids and solids. They exist between polar molecules, between ions and polar molecules, and between nonpolar molecules. A special type of intermolecular force, called the hydrogen bond, describes the interaction between the hydrogen atom in a polar bond and an electronegative atom such as O, N, or F.

**The Liquid State** Liquids tend to assume the shapes of their containers. The surface tension of a liquid is the energy required to increase its surface area. It manifests itself in capillary action, which is responsible for the rise (or depression) of a liquid in a narrow tubing. Viscosity is a measure of a liquid's resistance to flow. It always decreases with increasing temperature. The structure of water is unique in that its solid state (ice) is less dense than its liquid state.

**The Crystalline State** A crystalline solid possesses rigid and long-range order. Different crystal structures can be generated by packing identical spheres in three dimensions.

**Bonding in Solids** Atoms, molecules, or ions are held in a solid by different types of bonding. Electrostatic forces are responsible for ionic solids, intermolecular forces are responsible for molecular solids, covalent bonds are responsible for covalent solids, and a special type of interaction, which involves electrons being delocalized over the entire crystal, accounts for the existence of metals.

**Phase Transitions** The states of matter can be interconverted by heating or cooling. Two phases are in equilibrium at the transition temperature such as boiling or freezing. Solids can also be directly converted to vapor by sublimation. Above a certain temperature, called the critical temperature, the gas of a substance cannot be made to liquefy. The pressure-temperature relationships of solid, liquid, and vapor phases are best represented by a phase diagram.

**Interactive**



### Activity Summary

1. Animation: Packing Spheres (12.4)
2. Animation: Equilibrium Vapor Pressure (12.6)

## 12.1 The Kinetic Molecular Theory of Liquids and Solids

In Chapter 5 we used the kinetic molecular theory to explain the behavior of gases in terms of the constant, random motion of gas molecules. In gases, the distances between molecules are so great (compared with their diameters) that at ordinary temperatures and pressures (say, 25°C and 1 atm), there is no appreciable interaction between the molecules. Because there is a great deal of empty space in a gas—that is, space that is not occupied by molecules—gases can be readily compressed. The lack of strong forces between molecules also allows a gas to expand to fill the volume of its container. Furthermore, the large amount of empty space explains why gases have very low densities under normal conditions.

Liquids and solids are quite a different story. The principal difference between the condensed states (liquids and solids) and the gaseous state is the distance between molecules. In a liquid, the molecules are so close together that there is very little empty space. Thus, liquids are much more difficult to compress than gases, and they are also much denser under normal conditions. Molecules in a liquid are held together by one or more types of attractive forces, which will be discussed in Section 12.2. A liquid also has a definite volume, because molecules in a liquid do not break away from the attractive forces. The molecules can, however, move past one another freely, and so a liquid can flow, can be poured, and assumes the shape of its container.

In a solid, molecules are held rigidly in position with virtually no freedom of motion. Many solids are characterized by long-range order; that is, the molecules are arranged in regular configurations in three dimensions. There is even less empty space in a solid than in a liquid. Thus, solids are almost incompressible and possess definite shape and volume. With very few exceptions (water being the most important), the density of the solid form is higher than that of the liquid form for a given substance. It is not uncommon for two states of a substance to coexist. An ice cube (solid) floating in a glass of water (liquid) is a familiar example. Chemists refer to the different states of a substance that are present in a system as *phases*. Thus, our glass of ice water contains both the solid phase and the liquid phase of water. In this chapter we will use the term “phase” when talking about changes of state involving one substance, as well as systems containing more than one phase of a substance. Table 12.1 summarizes some of the characteristic properties of the three phases of matter.

**TABLE 12.1 Characteristic Properties of Gases, Liquids, and Solids**

| State of Matter | Volume/Shape   | Density | Compressibility            | Motion of Molecules           |
|-----------------|--|---------|----------------------------|-------------------------------|
| Gas             | Assumes the volume and shape of its container                | Low     | Very compressible          | Very free motion              |
| Liquid          | Has a definite volume but assumes the shape of its container | High    | Only slightly compressible | Slide past one another freely |
| Solid           | Has a definite volume and shape                              | High    | Virtually incompressible   | Vibrate about fixed positions |

## 12.2 Intermolecular Forces

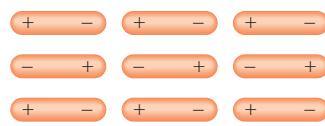
For simplicity we use the term “**intermolecular forces**” for both atoms and molecules.

**Intermolecular forces** are *attractive forces between molecules*. Intermolecular forces are responsible for the nonideal behavior of gases described in Chapter 5. They exert even more influence in the condensed phases of matter—liquids and solids. As the temperature of a gas drops, the average kinetic energy of its molecules decreases. Eventually, at a sufficiently low temperature, the molecules no longer have enough energy to break away from the attraction of neighboring molecules. At this point, the molecules aggregate to form small drops of liquid. This transition from the gaseous to the liquid phase is known as *condensation*.

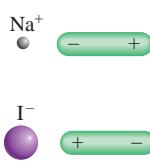
In contrast to intermolecular forces, *intramolecular forces hold atoms together in a molecule*. (Chemical bonding, discussed in Chapters 9 and 10, involves intramolecular forces.) Intramolecular forces stabilize individual molecules, whereas intermolecular forces are primarily responsible for the bulk properties of matter (for example, melting point and boiling point).

Generally, intermolecular forces are much weaker than intramolecular forces. Much less energy is usually required to evaporate a liquid than to break the bonds in the molecules of the liquid. For example, it takes about 41 kJ of energy to vaporize 1 mole of water at its boiling point; but about 930 kJ of energy are necessary to break the two O—H bonds in 1 mole of water molecules. The boiling points of substances often reflect the strength of the intermolecular forces operating among the molecules. At the boiling point, enough energy must be supplied to overcome the attractive forces among molecules before they can enter the vapor phase. If it takes more energy to separate molecules of substance A than of substance B because A molecules are held together by stronger intermolecular forces, then the boiling point of A is higher than that of B. The same principle applies also to the melting points of the substances. In general, the melting points of substances increase with the strength of the intermolecular forces.

To discuss the properties of condensed matter, we must understand the different types of intermolecular forces. *Dipole-dipole*, *dipole-induced dipole*, and *dispersion forces* make up what chemists commonly refer to as *van der Waals forces*, after the Dutch physicist Johannes van der Waals (see Section 5.8). Ions and dipoles are attracted to one another by electrostatic forces called *ion-dipole forces*, which are *not* van der Waals forces. *Hydrogen bonding* is a particularly strong type of dipole-dipole interaction. Because only a few elements can participate in hydrogen bond formation, it is treated as a separate category. Depending on the phase of a substance, the nature of chemical bonds, and the types of elements present, more than one type of interaction may contribute to the total attraction between molecules, as we will see below.



**Figure 12.1**  
Molecules that have a permanent dipole moment tend to align with opposite polarities in the solid phase for maximum attractive interaction.



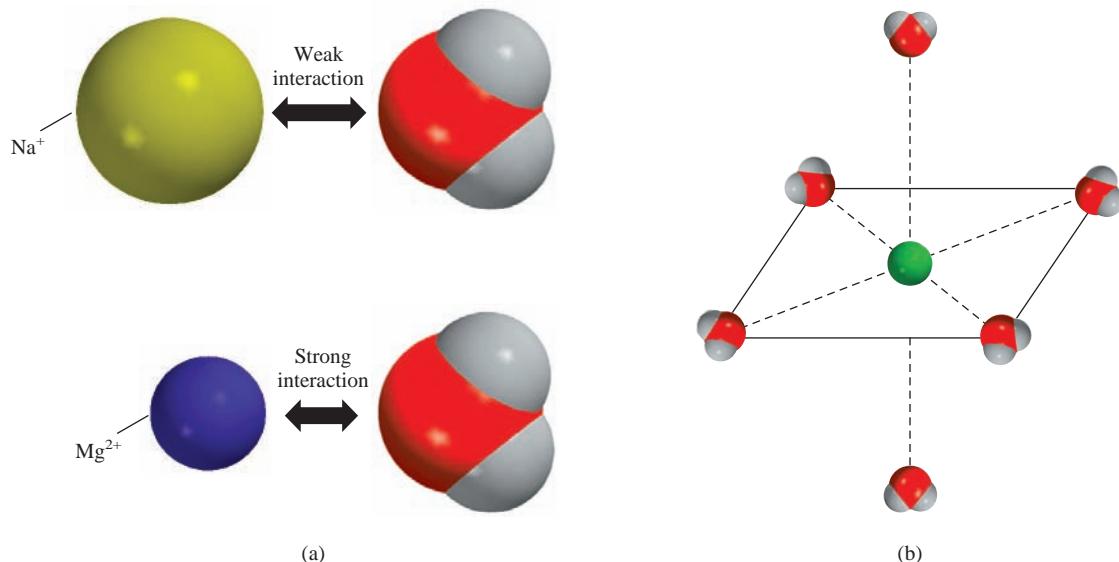
**Figure 12.2**  
Two types of ion-dipole interaction.

### Dipole-Dipole Forces

**Dipole-dipole forces** are *attractive forces between polar molecules*, that is, between molecules that possess dipole moments (see Section 10.2). Their origin is electrostatic, and they can be understood in terms of Coulomb’s law. The larger the dipole moment, the greater the force. Figure 12.1 shows the orientation of polar molecules in a solid. In liquids, polar molecules are not held as rigidly as in a solid, but they tend to align in a way that, on average, maximizes the attractive interaction.

### Ion-Dipole Forces

Coulomb’s law also explains *ion-dipole forces*, which attract an ion (either a cation or an anion) and a polar molecule to each other (Figure 12.2). The strength of this interaction depends on the charge and size of the ion and on the magnitude

**Figure 12.3**

(a) Interaction of a water molecule with a  $\text{Na}^+$  ion and a  $\text{Mg}^{2+}$  ion. (b) In aqueous solutions, metal ions are usually surrounded by six water molecules in an octahedral arrangement.

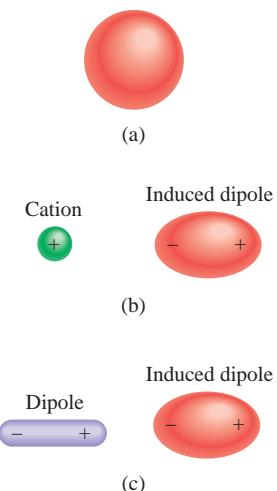
of the dipole moment and size of the molecule. The charges on cations are generally more concentrated, because cations are usually smaller than anions. Therefore, a cation interacts more strongly with dipoles than does an anion having a charge of the same magnitude.

Hydration, discussed in Section 4.1, is one example of ion-dipole interaction. Figure 12.3 shows the ion-dipole interaction between the  $\text{Na}^+$  and  $\text{Mg}^{2+}$  ions with a water molecule, which has a large dipole moment (1.87 D). Because the  $\text{Mg}^{2+}$  ion has a higher charge and a smaller ionic radius (78 pm) than that of the  $\text{Na}^+$  ion (98 pm), it interacts more strongly with water molecules. (In reality, each ion is surrounded by a number of water molecules in solution.) Similar differences exist for anions of different charges and sizes.

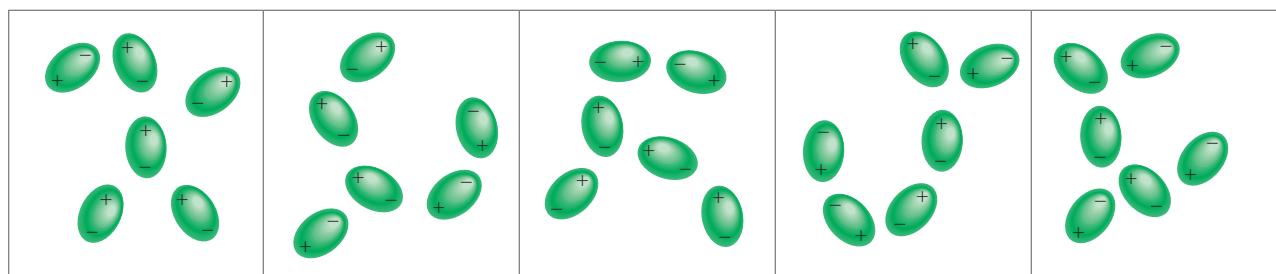
## Dispersion Forces

What attractive interaction occurs in nonpolar substances? To learn the answer to this question, consider the arrangement shown in Figure 12.4. If we place an ion or a polar molecule near an atom (or a nonpolar molecule), the electron distribution of the atom (or molecule) is distorted by the force exerted by the ion or the polar molecule, resulting in a kind of dipole. The dipole in the atom (or nonpolar molecule) is said to be an **induced dipole** because *the separation of positive and negative charges in the atom (or nonpolar molecule) is due to the proximity of an ion or a polar molecule*. The attractive interaction between an ion and the induced dipole is called **ion-induced dipole interaction**, and the attractive interaction between a polar molecule and the induced dipole is called **dipole-induced dipole interaction**.

The likelihood of a dipole moment being induced depends not only on the charge on the ion or the strength of the dipole but also on the **polarizability** of the atom or molecule—that is, *the ease with which the electron distribution in the atom (or molecule) can be distorted*. Generally, the larger the number of electrons and the more diffuse the electron cloud in the atom or molecule, the greater its polarizability. By

**Figure 12.4**

(a) Spherical charge distribution in a helium atom. (b) Distortion caused by the approach of a cation. (c) Distortion caused by the approach of a dipole.

**Figure 12.5**

*Induced dipoles interacting with each other. Such patterns exist only momentarily; new arrangements are formed in the next instant. This type of interaction is responsible for the condensation of nonpolar gases.*

*diffuse cloud* we mean an electron cloud that is spread over an appreciable volume, so that the electrons are not held tightly by the nucleus.

Polarizability allows gases containing atoms or nonpolar molecules (for example, He and N<sub>2</sub>) to condense. In a helium atom, the electrons are moving at some distance from the nucleus. At any instant it is likely that the atom has a dipole moment created by the specific positions of the electrons. This dipole moment is called an *instantaneous dipole* because it lasts for just a tiny fraction of a second. In the next instant, the electrons are in different locations and the atom has a new instantaneous dipole, and so on. Averaged over time (that is, the time it takes to make a dipole moment measurement), however, the atom has no dipole moment because the instantaneous dipoles all cancel one another. In a collection of He atoms, an instantaneous dipole of one He atom can induce a dipole in each of its nearest neighbors (Figure 12.5). At the next moment, a different instantaneous dipole can create temporary dipoles in the surrounding He atoms. The important point is that this kind of interaction produces **dispersion forces, attractive forces that arise as a result of temporary dipoles induced in atoms or molecules**. At very low temperatures (and reduced atomic speeds), dispersion forces are strong enough to hold He atoms together, causing the gas to condense. The attraction between nonpolar molecules can be explained similarly.

A quantum mechanical interpretation of temporary dipoles was provided by the German physicist Fritz London in 1930. London showed that the magnitude of this attractive interaction is directly proportional to the polarizability of the atom or molecule. As we might expect, dispersion forces may be quite weak. This is certainly true for helium, which has a boiling point of only 4.2 K, or  $-269^{\circ}\text{C}$ . (Note that helium has only two electrons, which are tightly held in the 1s orbital. Therefore, the helium atom has a low polarizability.)

Dispersion forces, which are also called London forces, usually increase with molar mass because molecules with larger molar mass tend to have more electrons, and dispersion forces increase in strength with the number of electrons. Furthermore, larger molar mass often means a bigger atom whose electron distribution is more easily disturbed because the outer electrons are less tightly held by the nuclei. Table 12.2 compares the melting points of similar substances that consist of nonpolar molecules. As expected, the melting point increases as the number of electrons in the molecule increases. Because these are all nonpolar molecules, the only attractive intermolecular forces present are the dispersion forces.

In many cases, dispersion forces are comparable to or even greater than the dipole-dipole forces between polar molecules. For a dramatic illustration, let us compare the boiling points of CH<sub>3</sub>F ( $-78.4^{\circ}\text{C}$ ) and CCl<sub>4</sub> ( $76.5^{\circ}\text{C}$ ). Although CH<sub>3</sub>F has a dipole moment of 1.8 D, it boils at a much lower temperature than CCl<sub>4</sub>, a nonpolar

**TABLE 12.2**
**Melting Points of Similar Nonpolar Compounds**

| Compound         | Melting Point (°C) |
|------------------|--------------------|
| CH <sub>4</sub>  | -182.5             |
| CF <sub>4</sub>  | -150.0             |
| CCl <sub>4</sub> | -23.0              |
| CBr <sub>4</sub> | 90.0               |
| CI <sub>4</sub>  | 171.0              |

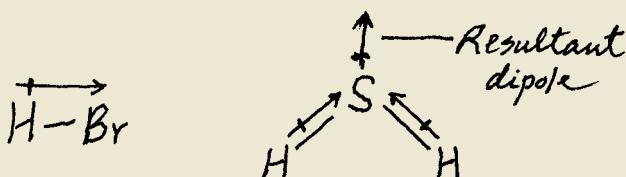
molecule.  $\text{CCl}_4$  boils at a higher temperature simply because it contains more electrons. As a result, the dispersion forces between  $\text{CCl}_4$  molecules are stronger than the dispersion forces plus the dipole-dipole forces between  $\text{CH}_3\text{F}$  molecules. (Keep in mind that dispersion forces exist among species of all types, whether they are neutral or bear a net charge and whether they are polar or nonpolar.)

### Example 12.1

What type(s) of intermolecular forces exist between the following pairs: (a) HBr and  $\text{H}_2\text{S}$ , (b)  $\text{Cl}_2$  and  $\text{CBr}_4$ , (c)  $\text{I}_2$  and  $\text{NO}_3^-$ , (d)  $\text{NH}_3$  and  $\text{C}_6\text{H}_6$ ?

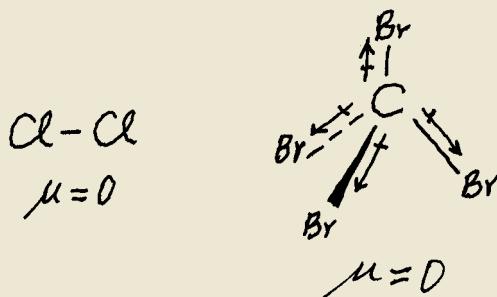
**Strategy** Classify the species into three categories: ionic, polar (possessing a dipole moment), and nonpolar. Keep in mind that dispersion forces exist between *all* species.

**Solution** (a) Both HBr and  $\text{H}_2\text{S}$  are polar molecules.



Therefore, the intermolecular forces present are dipole-dipole forces, as well as dispersion forces.

(b) Both  $\text{Cl}_2$  and  $\text{CBr}_4$  are nonpolar, so there are only dispersion forces between these molecules.



- (c)  $\text{I}_2$  is a homonuclear diatomic molecule and therefore nonpolar, so the forces between it and the ion  $\text{NO}_3^-$  are ion-induced dipole forces and dispersion forces.  
 (d)  $\text{NH}_3$  is polar, and  $\text{C}_6\text{H}_6$  is nonpolar. The forces are dipole-induced dipole forces and dispersion forces.

**Similar problem:** 12.10.

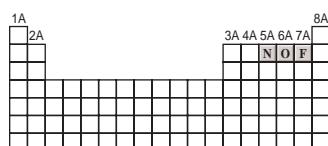
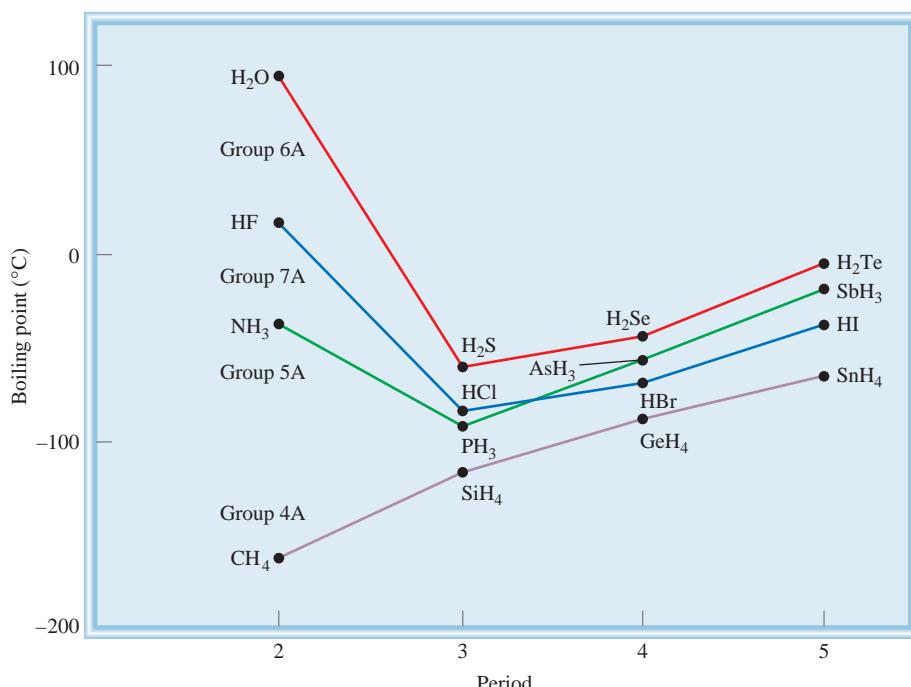
**Practice Exercise** Name the type(s) of intermolecular forces that exists between molecules (or basic units) in each of the following species: (a) LiF, (b)  $\text{CH}_4$ , (c)  $\text{SO}_2$ .

## The Hydrogen Bond

Normally, the boiling points of a series of similar compounds containing elements in the same periodic group increase with increasing molar mass. This increase in boiling point is due to the increase in dispersion forces for molecules with more electrons. Hydrogen compounds of Group 4A follow this trend, as Figure 12.6 shows. The lightest compound,  $\text{CH}_4$ , has the lowest boiling point, and the heaviest compound,  $\text{SnH}_4$ , has the highest boiling point. However, hydrogen compounds of the elements in Groups 5A, 6A, and 7A do not follow this trend. In each of these series, the lightest

**Figure 12.6**

*Boiling points of the hydrogen compounds of Groups 4A, 5A, 6A, and 7A elements. Although normally we expect the boiling point to increase as we move down a group, we see that three compounds ( $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{HF}$ ) behave differently. The anomaly can be explained in terms of intermolecular hydrogen bonding.*



The three most electronegative elements that take part in hydrogen bonding.

compound ( $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{HF}$ ) has the highest boiling point, contrary to our expectations based on molar mass. This observation must mean that there are stronger intermolecular attractions in  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{HF}$ , compared to other molecules in the same groups. In fact, this particularly strong type of intermolecular attraction is called the **hydrogen bond**, which is a special type of dipole-dipole interaction between the hydrogen atom in a polar bond, such as  $\text{N}-\text{H}$ ,  $\text{O}-\text{H}$ , or  $\text{F}-\text{H}$ , and an electronegative  $\text{O}$ ,  $\text{N}$ , or  $\text{F}$  atom. The interaction is written

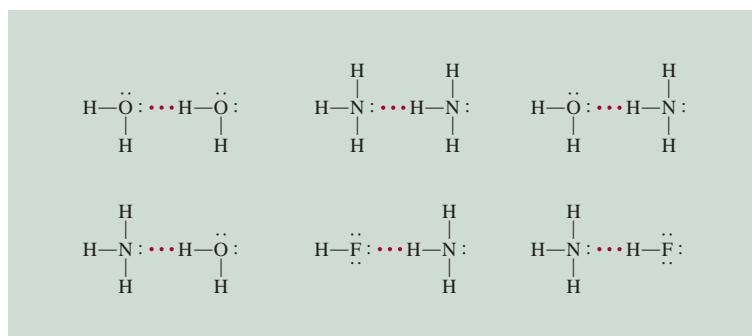


A and B represent O, N, or F; A—H is one molecule or part of a molecule and B is a part of another molecule; and the dotted line represents the hydrogen bond. The three atoms usually lie in a straight line, but the angle AHB (or AHA) can deviate as much as  $30^\circ$  from linearity. Note that the O, N, and F atoms all possess at least one lone pair that can interact with the hydrogen atom in hydrogen bonding.

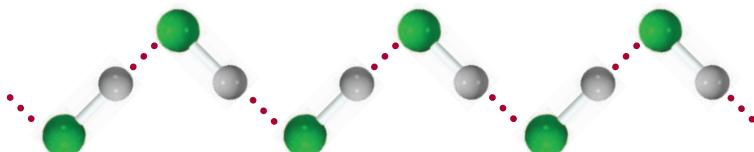
The average energy of a hydrogen bond is quite large for a dipole-dipole interaction (up to 40 kJ/mol). Thus, hydrogen bonds have a powerful effect on the structures and properties of many compounds. Figure 12.7 shows several examples of hydrogen bonding.

**Figure 12.7**

*Hydrogen bonding in water, ammonia, and hydrogen fluoride. Solid lines represent covalent bonds, and dotted lines represent hydrogen bonds.*



The strength of a hydrogen bond is determined by the coulombic interaction between the lone-pair electrons of the electronegative atom and the hydrogen nucleus. For example, fluorine is more electronegative than oxygen, and so we would expect a stronger hydrogen bond to exist in liquid HF than in H<sub>2</sub>O. In the liquid phase, the HF molecules form zigzag chains:



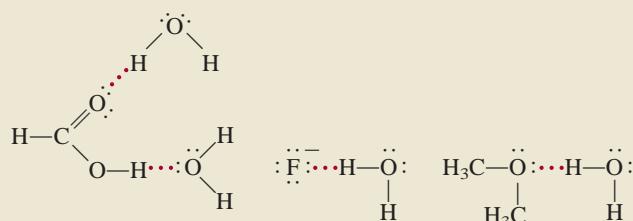
The boiling point of HF is lower than that of water because each H<sub>2</sub>O takes part in *four* intermolecular hydrogen bonds. Therefore, the forces holding the molecules together are stronger in H<sub>2</sub>O than in HF. We will return to this very important property of water in Section 12.3.

### Example 12.2

Which of the following can form hydrogen bonds with water? CH<sub>3</sub>OCH<sub>3</sub>, CH<sub>4</sub>, F<sup>-</sup>, HCOOH, Na<sup>+</sup>.

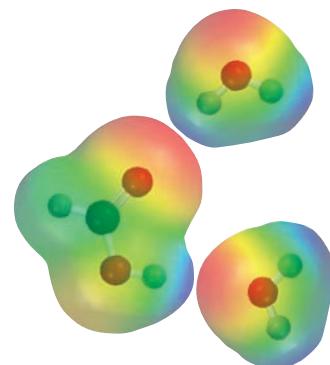
**Strategy** A species can form hydrogen bonds with water if it contains one of the three electronegative elements (F, O, or N) or it has an H atom bonded to one of these three elements.

**Solution** There are no electronegative elements (F, O, or N) in either CH<sub>4</sub> or Na<sup>+</sup>. Therefore, only CH<sub>3</sub>OCH<sub>3</sub>, F<sup>-</sup>, and HCOOH can form hydrogen bonds with water.



**Check** Note that HCOOH (formic acid) can form hydrogen bonds with water in two different ways.

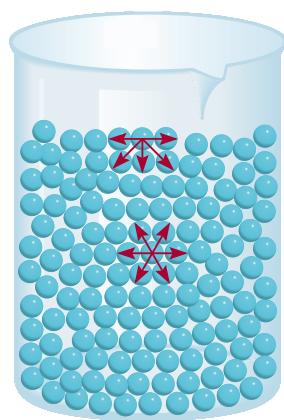
**Practice Exercise** Which of the following species are capable of hydrogen bonding among themselves? (a) H<sub>2</sub>S, (b) C<sub>6</sub>H<sub>6</sub>, (c) CH<sub>3</sub>OH.



HCOOH forms hydrogen bonds with two H<sub>2</sub>O molecules.

**Similar problem: 12.12.**

The intermolecular forces discussed so far are all attractive in nature. Keep in mind, though, that molecules also exert repulsive forces on one another. Thus, when two molecules approach each other, the repulsion between the electrons and between the nuclei in the molecules comes into play. The magnitude of the repulsive force rises very steeply as the distance separating the molecules in a condensed phase decreases. This is the reason that liquids and solids are so hard to compress. In these phases, the molecules are already in close contact with one another, and so they greatly resist being compressed further.

**Figure 12.8**

*Intermolecular forces acting on a molecule in the surface layer of a liquid and in the interior region of the liquid.*



Surface tension enables the water strider to “walk” on water.

**Figure 12.9**

*Water beads on an apple, which has a waxy surface.*

## 12.3 Properties of Liquids

Intermolecular forces give rise to a number of structural features and properties of liquids. In this section we will look at two such phenomena associated with liquids in general: surface tension and viscosity. Then we will discuss the structure and properties of water.

### Surface Tension

Molecules within a liquid are pulled in all directions by intermolecular forces; there is no tendency for them to be pulled in any one way. However, molecules at the surface are pulled downward and sideways by other molecules, but not upward away from the surface (Figure 12.8). These intermolecular attractions thus tend to pull the molecules into the liquid and cause the surface to tighten like an elastic film. Because there is little or no attraction between polar water molecules and, say, the nonpolar wax molecules on a freshly waxed car, a drop of water assumes the shape of a small round bead, because a sphere minimizes the surface area of a liquid. The waxy surface of a wet apple also produces this effect (Figure 12.9).

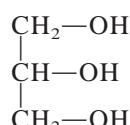
A measure of the elastic force in the surface of a liquid is surface tension. The **surface tension** is the amount of energy required to stretch or increase the surface of a liquid by a unit area (for example, by  $1 \text{ cm}^2$ ). Liquids that have strong intermolecular forces also have high surface tensions. Thus, because of hydrogen bonding, water has a considerably greater surface tension than most other liquids.

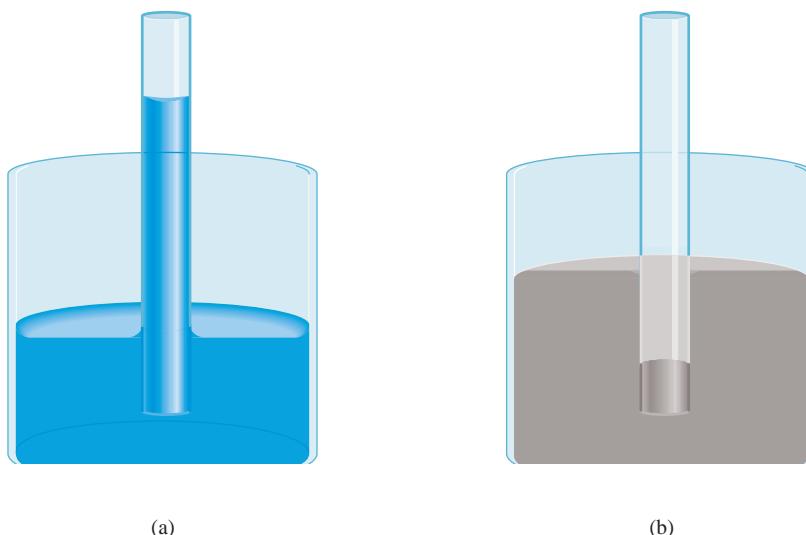
Another example of surface tension is *capillary action*. Figure 12.10(a) shows water rising spontaneously in a capillary tube. A thin film of water adheres to the wall of the glass tube. The surface tension of water causes this film to contract, and as it does, it pulls the water up the tube. Two types of forces bring about capillary action. One is **cohesion**, which is the intermolecular attraction between like molecules (in this case, the water molecules). The second force, called **adhesion**, is an attraction between unlike molecules, such as those in water and in the sides of a glass tube. If adhesion is stronger than cohesion, as it is in Figure 12.10(a), the contents of the tube will be pulled upward. This process continues until the adhesive force is balanced by the weight of the water in the tube. This action is by no means universal among liquids, as Figure 12.10(b) shows. In mercury, cohesion is greater than the adhesion between mercury and glass, so that when a capillary tube is dipped in mercury, the result is a depression or lowering, at the mercury level—that is, the height of the liquid in the capillary tube is below the surface of the mercury.

### Viscosity

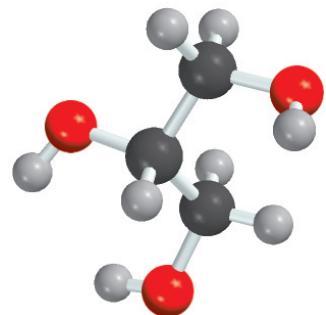
The expression “slow as molasses in January” owes its truth to another physical property of liquids called viscosity. **Viscosity** is a measure of a fluid’s resistance to flow. The greater the viscosity, the more slowly the liquid flows. The viscosity of a liquid usually decreases as temperature increases; thus, hot molasses flows much faster than cold molasses.

Liquids that have strong intermolecular forces have higher viscosities than those that have weak intermolecular forces (Table 12.3). Water has a higher viscosity than many other liquids because of its ability to form hydrogen bonds. Interestingly, the viscosity of glycerol is significantly higher than that of all the other liquids listed in Table 12.3. Glycerol has the structure



**Figure 12.10**

(a) When adhesion is greater than cohesion, the liquid (for example, water) rises in the capillary tube. (b) When cohesion is greater than adhesion, as it is for mercury, a depression of the liquid in the capillary tube results. Note that the meniscus in the tube of water is concave, or rounded downward, whereas that in the tube of mercury is convex, or rounded upward.



Like water, glycerol can form hydrogen bonds. Each glycerol molecule has three —OH groups that can participate in hydrogen bonding with other glycerol molecules. Furthermore, because of their shape, the molecules have a great tendency to become entangled rather than to slip past one another as the molecules of less viscous liquids do. These interactions contribute to its high viscosity.

## The Structure and Properties of Water

Water is so common a substance on Earth that we often overlook its unique nature. All life processes involve water. Water is an excellent solvent for many ionic compounds, as well as for other substances capable of forming hydrogen bonds with water.

As Table 6.2 shows, water has a high specific heat. The reason is that to raise the temperature of water (that is, to increase the average kinetic energy of water molecules), we must first break the many intermolecular hydrogen bonds. Thus, water can absorb a substantial amount of heat while its temperature rises only slightly. The converse is also true: Water can give off much heat with only a slight decrease in its temperature. For this reason, the huge quantities of water that are present in our lakes

Glycerol is a clear, odorless, syrupy liquid used to make explosives, ink, and lubricants.

If water did not have the ability to form hydrogen bonds, it would be a gas at room temperature.

**TABLE 12.3 Viscosity of Some Common Liquids at 20°C**

| Liquid  | Viscosity (N s/m <sup>2</sup> )* |
|---|----------------------------------|
| Acetone (C <sub>3</sub> H <sub>6</sub> O)                                     | 3.16 × 10 <sup>-4</sup>          |
| Benzene (C <sub>6</sub> H <sub>6</sub> )                                      | 6.25 × 10 <sup>-4</sup>          |
| Blood   | 4 × 10 <sup>-3</sup>             |
| Carbon tetrachloride (CCl <sub>4</sub> )                                      | 9.69 × 10 <sup>-4</sup>          |
| Diethyl ether (C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub> ) | 2.33 × 10 <sup>-4</sup>          |
| Ethanol (C <sub>2</sub> H <sub>5</sub> OH)                                    | 1.20 × 10 <sup>-3</sup>          |
| Glycerol (C <sub>3</sub> H <sub>8</sub> O <sub>3</sub> )                      | 1.49                             |
| Mercury (Hg)  | 1.55 × 10 <sup>-3</sup>          |
| Water (H <sub>2</sub> O)  | 1.01 × 10 <sup>-3</sup>          |

\* The SI units of viscosity are newton-second per meter squared.

**Figure 12.11**

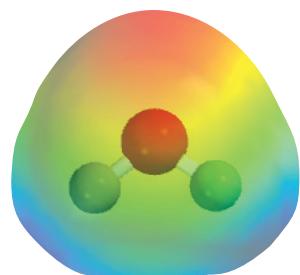
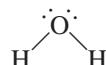
*Left: Ice cubes float on water.  
Right: Solid benzene sinks to the bottom of liquid benzene.*



and oceans can effectively moderate the climate of adjacent land areas by absorbing heat in the summer and giving off heat in the winter, with only small changes in the temperature of the body of water.

The most striking property of water is that its solid form is less dense than its liquid form: ice floats at the surface of liquid water. The density of almost all other substances is greater in the solid state than in the liquid state (Figure 12.11).

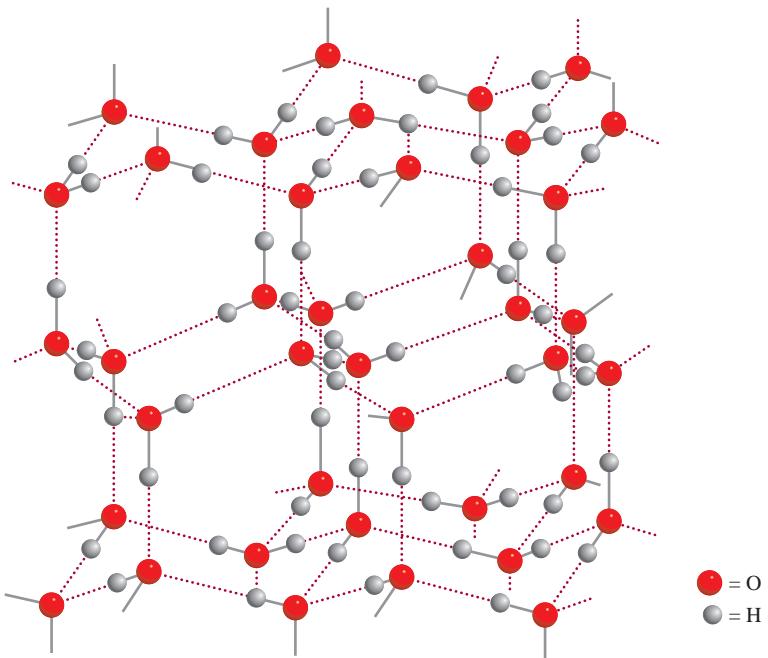
To understand why water is different, we have to examine the electronic structure of the  $\text{H}_2\text{O}$  molecule. As we saw in Chapter 9, there are two pairs of nonbonding electrons, or two lone pairs, on the oxygen atom:



Electrostatic potential map of water.

Although many compounds can form intermolecular hydrogen bonds, the difference between  $\text{H}_2\text{O}$  and other polar molecules, such as  $\text{NH}_3$  and  $\text{HF}$ , is that each oxygen atom can form *two* hydrogen bonds, the same as the number of lone electron pairs on the oxygen atom. Thus, water molecules are joined together in an extensive three-dimensional network in which each oxygen atom is approximately tetrahedrally bonded to four hydrogen atoms, two by covalent bonds and two by hydrogen bonds. This equality in the number of hydrogen atoms and lone pairs is not characteristic of  $\text{NH}_3$  or  $\text{HF}$  or, for that matter, of any other molecule capable of forming hydrogen bonds. Consequently, these other molecules can form rings or chains, but not three-dimensional structures.

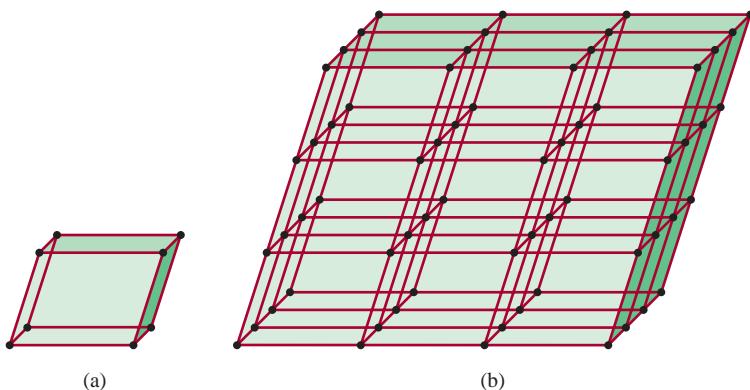
The highly ordered three-dimensional structure of ice (Figure 12.12) prevents the molecules from getting too close to one another. But consider what happens when ice melts. At the melting point, a number of water molecules have enough kinetic energy to break free of the intermolecular hydrogen bonds. These molecules become trapped in the cavities of the three-dimensional structure, which is broken down into smaller clusters. As a result, there are more molecules per unit volume in liquid water than in ice. Thus, because density = mass/volume, the density of water is greater than that of ice. With further heating, more water molecules are released from intermolecular hydrogen bonding, so that the density of water tends to increase with rising temperature just above the melting point. Of course, at the same time, water expands as it is being heated so that its density is decreased. These two processes—the trapping of free water molecules in cavities and thermal expansion—act in opposite directions. From  $0^\circ\text{C}$  to  $4^\circ\text{C}$ , the trapping prevails and water becomes progressively denser. Beyond  $4^\circ\text{C}$ , however, thermal expansion predominates and the density of water decreases with increasing temperature (Figure 12.13).



## 12.4 Crystal Structure

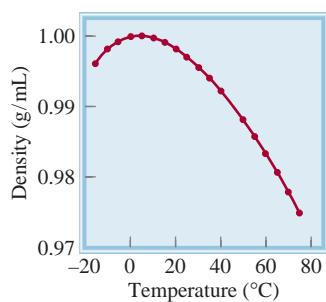
Solids can be divided into two categories: crystalline and amorphous. Ice is a ***crystalline solid***, which *possesses rigid and long-range order; its atoms, molecules, or ions occupy specific positions*. The arrangement of atoms, molecules, or ions in a crystalline solid is such that the net attractive intermolecular forces are at their maximum. The forces responsible for the stability of any crystal can be ionic forces, covalent bonds, van der Waals forces, hydrogen bonds, or a combination of these forces. ***Amorphous solids***, such as glass, lack a well-defined arrangement and long-range molecular order. In this section we will concentrate on the structure of crystalline solids.

The basic repeating structural unit of a crystalline solid is a **unit cell**. Figure 12.14 shows a unit cell and its extension in three dimensions. Each sphere represents an atom, an ion, or a molecule and is called a **lattice point**. In many crystals, the lattice point does not actually contain an atom, ion, or molecule. Rather, there may be several atoms, ions, or molecules identically arranged about each lattice point. For simplicity, however, we can assume that each lattice point is occupied by an atom.



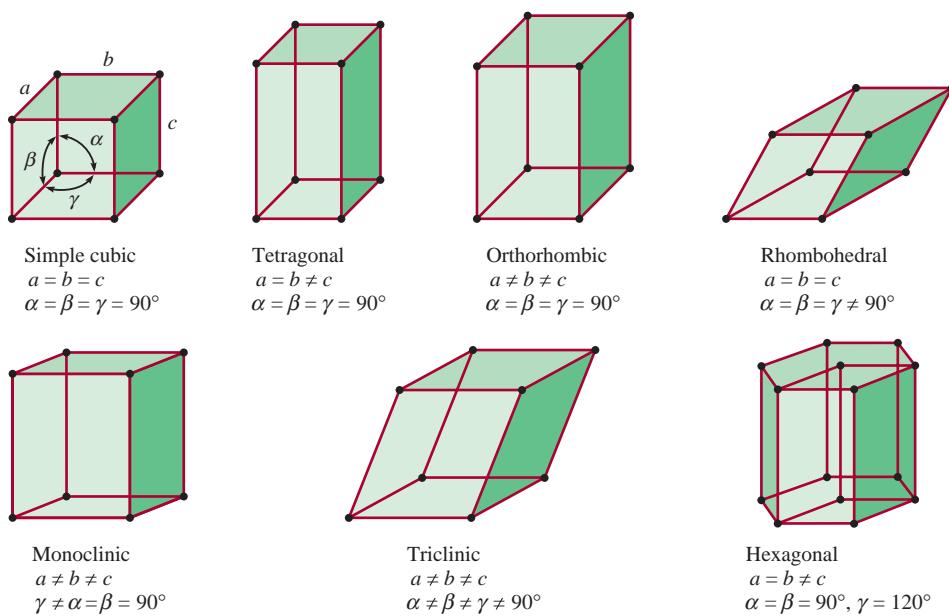
**Figure 12.12**

The three-dimensional structure of ice. Each O atom is bonded to four H atoms. The covalent bonds are shown by short solid lines and the weaker hydrogen bonds by long dotted lines between O and H. The empty space in the structure accounts for the low density of ice.



**Figure 12.13**

*Plot of density versus temperature for liquid water. The maximum density of water is reached at 4°C. The density of ice at 0°C is about 0.92 g/cm<sup>3</sup>.*

**Figure 12.15**

The seven types of unit cells. Angle  $\alpha$  is defined by edges  $b$  and  $c$ , angle  $\beta$  by edges  $a$  and  $c$ , and angle  $\gamma$  by edges  $a$  and  $b$ .

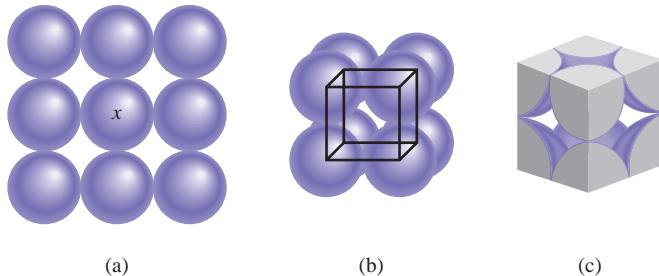
Every crystalline solid can be described in terms of one of the seven types of unit cells shown in Figure 12.15. The geometry of the cubic unit cell is particularly simple because all sides and all angles are equal. Any of the unit cells, when repeated in space in all three dimensions, forms the lattice structure characteristic of a crystalline solid.

## Packing Spheres

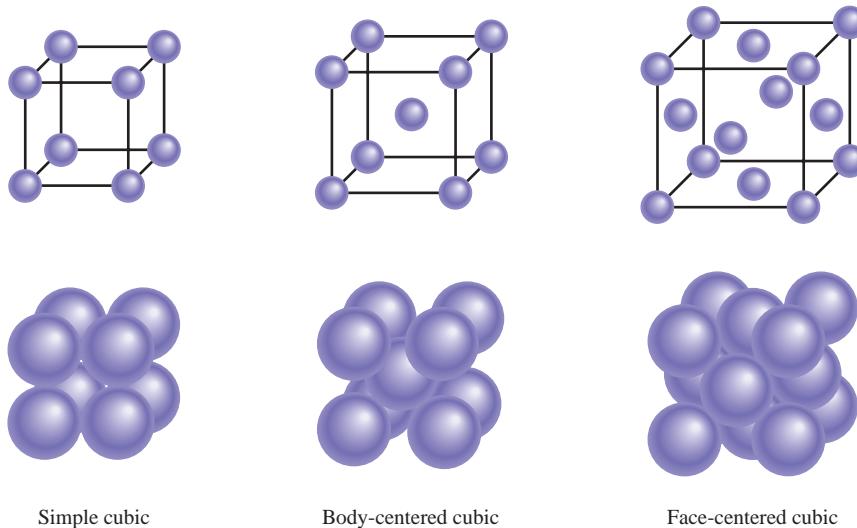


We can understand the general geometric requirements for crystal formation by considering the different ways of packing a number of identical spheres (Ping-Pong balls, for example) to form an ordered three-dimensional structure. The way the spheres are arranged in layers determines what type of unit cell we have.

In the simplest case, a layer of spheres can be arranged as shown in Figure 12.16(a). The three-dimensional structure can be generated by placing a layer above and below this layer in such a way that spheres in one layer are directly over the spheres in the

**Figure 12.16**

Arrangement of identical spheres in a simple cubic cell. (a) Top view of one layer of spheres. (b) Definition of a simple cubic cell. (c) Because each sphere is shared by eight unit cells and there are eight corners in a cube, there is the equivalent of one complete sphere inside a simple cubic unit cell.

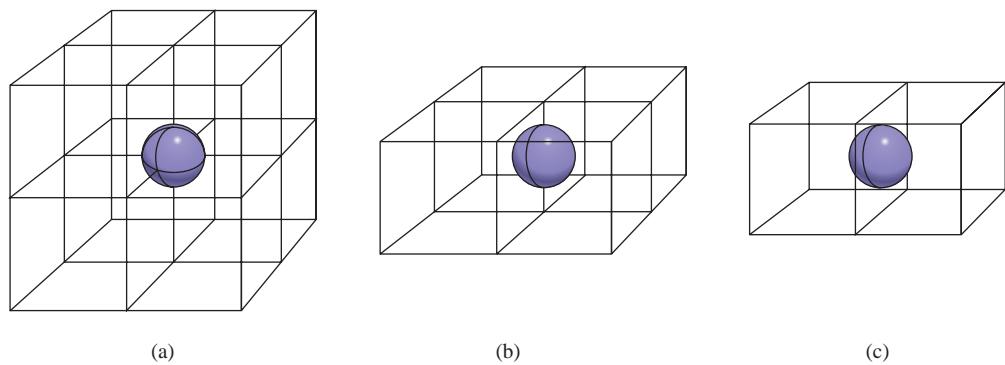


**Figure 12.17**  
Three types of cubic cells. In reality, the spheres representing atoms, molecules, or ions are in contact with one another in these cubic cells.

layer below it. This procedure can be extended to generate many, many layers, as in the case of a crystal. Focusing on the sphere marked with  $x$ , we see that it is in contact with four spheres in its own layer, one sphere in the layer above, and one sphere in the layer below. Each sphere in this arrangement is said to have a coordination number of 6 because it has six immediate neighbors. The ***coordination number*** is defined as *the number of atoms (or ions) surrounding an atom (or ion) in a crystal lattice*. The basic, repeating unit in this array of spheres is called a ***simple cubic cell (sc)*** [Figure 12.16(b)].

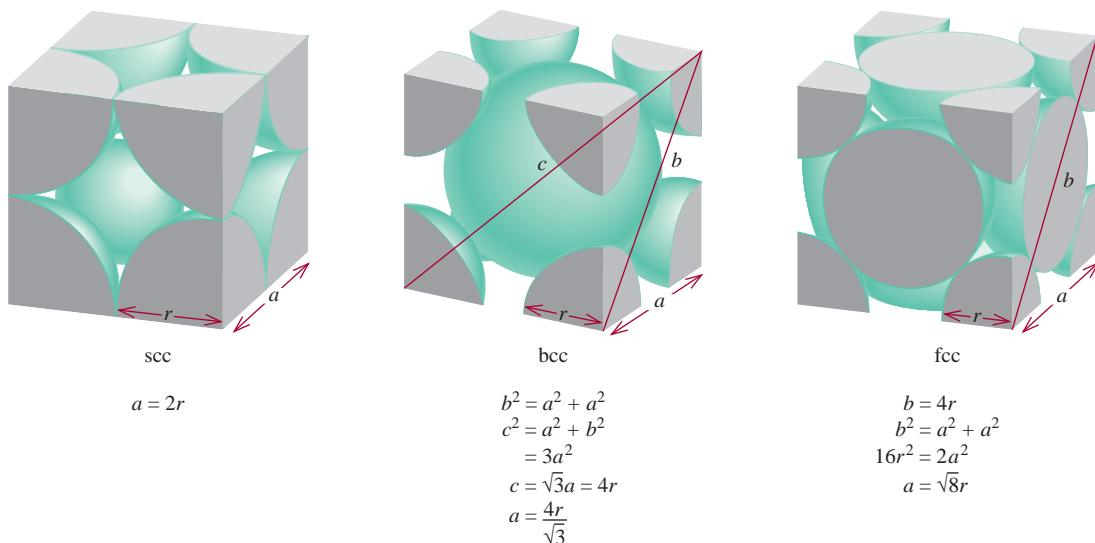
The other types of cubic cells are the *body-centered cubic cell* (bcc) and the *face-centered cubic cell* (fcc) (Figure 12.17). A body-centered cubic arrangement differs from a simple cube in that the second layer of spheres fits into the depressions of the first layer and the third layer into the depressions of the second layer. The coordination number of each sphere in this structure is 8 (each sphere is in contact with four spheres in the layer above and four spheres in the layer below). In the face-centered cubic cell there are spheres at the center of each of the six faces of the cube in addition to the eight corner spheres and the coordination number of each sphere is 12.

Because every unit cell in a crystalline solid is adjacent to other unit cells, most of a cell's atoms are shared by neighboring cells. For example, in all types of cubic cells, each corner atom belongs to eight unit cells [Figure 12.18(a)]; an



**Figure 12.18**

(a) A corner atom in any cell is shared by eight unit cells. (b) An edge atom is shared by four unit cells. (c) A face-centered atom in a cubic cell is shared by two unit cells.

**Figure 12.19**

The relationship between the edge length ( $a$ ) and radius ( $r$ ) of atoms in the simple cubic cell (sc), body-centered cubic cell (bcc), and face-centered cubic cell (fcc).

edge atom is shared by four unit cells [Figure 12.18(b)], and a face-centered atom is shared by two unit cells [Figure 12.18(c)]. Because each corner sphere is shared by eight unit cells and there are eight corners in a cube, there will be the equivalent of only one complete sphere inside a simple cubic unit cell (Figure 12.19). A body-centered cubic cell contains the equivalent of two complete spheres, one in the center and eight shared corner spheres. A face-centered cubic cell contains four complete spheres—three from the six face-centered atoms and one from the eight shared corner spheres.

Figure 12.19 also summarizes the relationship between the atomic radius  $r$  and the edge length  $a$  of a simple cubic cell, a body-centered cubic cell, and a face-centered cubic cell. This relationship can be used to determine the density of a crystal, as Example 12.3 shows.

### Example 12.3

Gold (Au) crystallizes in a cubic close-packed structure (the face-centered cubic unit cell) and has a density of 19.3 g/cm<sup>3</sup>. Calculate the atomic radius of gold in picometers.

**Strategy** We want to calculate the radius of a gold atom. For a face-centered cubic unit cell, the relationship between radius ( $r$ ) and edge length ( $a$ ), according to Figure 12.19, is  $a = \sqrt{8}r$ . Therefore, to determine  $r$  of a Au atom, we need to find  $a$ . The volume of a cube is  $V = a^3$  or  $a = \sqrt[3]{V}$ . Thus, if we can determine the volume of the unit cell, we can calculate  $a$ . We are given the density in the problem.

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

need to find  
want to calculate

given

(Continued)

The sequence of steps is summarized as follows:

density of unit cell → volume of unit cell → edge length of unit cell → radius of Au atom

### Solution

*Step 1:* We know the density, so in order to determine the volume, we find the mass of the unit cell. Each unit cell has eight corners and six faces. The total number of atoms within such a cell, according to Figure 12.18, is

$$\left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4$$

The mass of a unit cell in grams is

$$\begin{aligned} m &= \frac{4 \text{ atoms}}{1 \text{ unit cell}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{197.0 \text{ g Au}}{1 \text{ mol Au}} \\ &= 1.31 \times 10^{-21} \text{ g/unit cell} \end{aligned}$$

From the definition of density ( $d = m/V$ ), we calculate the volume of the unit cell as follows:

$$V = \frac{m}{d} = \frac{1.31 \times 10^{-21} \text{ g}}{19.3 \text{ g/cm}^3} = 6.79 \times 10^{-23} \text{ cm}^3$$

*Step 2:* Because volume is length cubed, we take the cubic root of the volume of the unit cell to obtain the edge length ( $a$ ) of the cell

$$\begin{aligned} a &= \sqrt[3]{V} \\ &= \sqrt[3]{6.79 \times 10^{-23} \text{ cm}^3} \\ &= 4.08 \times 10^{-8} \text{ cm} \end{aligned}$$

*Step 3:* From Figure 12.19 we see that the radius of an Au sphere ( $r$ ) is related to the edge length by

$$a = \sqrt{8r}$$

Therefore,

$$\begin{aligned} r &= \frac{a}{\sqrt{8}} = \frac{4.08 \times 10^{-8} \text{ cm}}{\sqrt{8}} \\ &= 1.44 \times 10^{-8} \text{ cm} \\ &= 1.44 \times 10^{-8} \text{ cm} \times \frac{1 \times 10^{-2} \text{ m}}{1 \text{ cm}} \times \frac{1 \text{ pm}}{1 \times 10^{-12} \text{ m}} \\ &= 144 \text{ pm} \end{aligned}$$

Remember that density is an intensive property, so that it is the same for one unit cell and 1 cm<sup>3</sup> of the substance.

Similar problem: 12.48.

**Practice Exercise** When silver crystallizes, it forms face-centered cubic cells. The unit cell edge length is 408.7 pm. Calculate the density of silver.

## 12.5 Bonding in Solids

The structure and properties of crystalline solids, such as melting point, density, and hardness, are determined by the attractive forces that hold the particles together. We can classify crystals according to the types of forces between particles: ionic, molecular, covalent, and metallic (Table 12.4).

**TABLE 12.4** Types of Crystals and General Properties

| Type of Crystal | Force(s) Holding the Units Together                     | General Properties  | Examples   |
|-----------------|---|---|--|
| Ionic           | Electrostatic attraction                                | Hard, brittle, high melting point, poor conductor of heat and electricity       | NaCl, LiF, MgO, CaCO <sub>3</sub>  |
| Molecular*      | Dispersion forces, dipole-dipole forces, hydrogen bonds | Soft, low melting point, poor conductor of heat and electricity                 | Ar, CO <sub>2</sub> , I <sub>2</sub> , H <sub>2</sub> O, C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> (sucrose) |
| Covalent        | Covalent bond   | Hard, high melting point, poor conductor of heat and electricity                | C (diamond), <sup>†</sup> SiO <sub>2</sub> (quartz)  |
| Metallic        | Metallic bond   | Soft to hard, low to high melting point, good conductor of heat and electricity | All metallic elements; for example, Na, Mg, Fe, Cu   |

\*Included in this category are crystals made up of individual atoms.

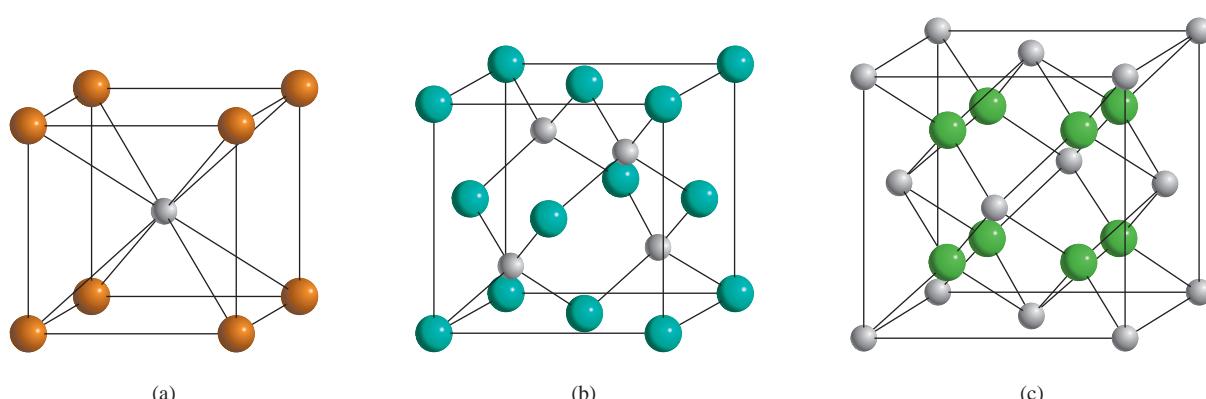
<sup>†</sup>Diamond is a good thermal conductor.



These giant ionic potassium dihydrogen phosphate crystals were grown in the laboratory. The largest one weighs 701 lb!

## Ionic Crystals

Ionic crystals consist of ions held together by ionic bonds. The structure of an ionic crystal depends on the charges on the cation and anion and on their radii. We have already discussed the structure of sodium chloride, which has a face-centered cubic lattice (see Figure 2.12). Figure 12.20 shows the structures of three other ionic crystals: CsCl, ZnS, and CaF<sub>2</sub>. Because Cs<sup>+</sup> is considerably larger than Na<sup>+</sup>, CsCl has the simple cubic lattice structure. ZnS has the *zincblende* structure, which is based on the face-centered cubic lattice. If the S<sup>2-</sup> ions are located at the lattice points, the Zn<sup>2+</sup> ions are located one-fourth of the distance along each body diagonal. Other ionic compounds that have the zincblende structure include CuCl, BeS, CdS, and HgS. CaF<sub>2</sub> has the *fluorite* structure. The Ca<sup>2+</sup> ions are located at the lattice points, and each F<sup>-</sup> ion is tetrahedrally surrounded by four Ca<sup>2+</sup> ions. The compounds SrF<sub>2</sub>, BaF<sub>2</sub>, BaCl<sub>2</sub>, and PbF<sub>2</sub> also have the fluorite structure.

**Figure 12.20**

Crystal structures of (a) CsCl, (b) ZnS, and (c) CaF<sub>2</sub>. In each case, the cation is the smaller sphere.

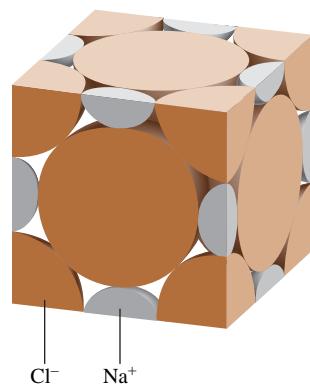
Ionic solids have high melting points, an indication of the strong cohesive force holding the ions together. These solids do not conduct electricity because the ions are fixed in position. However, in the molten state (that is, when melted) or dissolved in water, the ions are free to move and the resulting liquid is electrically conducting.

### Example 12.4

How many  $\text{Na}^+$  and  $\text{Cl}^-$  ions are in each  $\text{NaCl}$  unit cell?

**Solution**  $\text{NaCl}$  has a structure based on a face-centered cubic lattice. As Figure 2.12 shows, one whole  $\text{Na}^+$  ion is at the center of the unit cell, and there are 12  $\text{Na}^+$  ions at the edges. Because each edge  $\text{Na}^+$  ion is shared by four unit cells, the total number of  $\text{Na}^+$  ions is  $1 + (12 \times \frac{1}{4}) = 4$ . Similarly, there are six  $\text{Cl}^-$  ions at the face centers and eight  $\text{Cl}^-$  ions at the corners. Each face-centered ion is shared by two unit cells, and each corner ion is shared by eight unit cells (see Figure 12.18), so the total number of  $\text{Cl}^-$  ions is  $(6 \times \frac{1}{2}) + (8 \times \frac{1}{8}) = 4$ . Thus, there are four  $\text{Na}^+$  ions and four  $\text{Cl}^-$  ions in each  $\text{NaCl}$  unit cell. Figure 12.21 shows the portions of the  $\text{Na}^+$  and  $\text{Cl}^-$  ions within a unit cell.

**Practice Exercise** How many atoms are in a body-centered cube, assuming that all atoms occupy lattice points?



**Figure 12.21**

*Portions of  $\text{Na}^+$  and  $\text{Cl}^-$  ions within a face-centered cubic unit cell.*

**Similar problem: 12.47.**

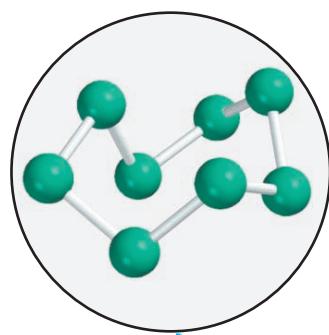
## Molecular Crystals

Molecular crystals consist of atoms or molecules held together by van der Waals forces and/or hydrogen bonding. An example of a molecular crystal is solid sulfur dioxide ( $\text{SO}_2$ ), in which the predominant attractive force is dipole-dipole interaction. Intermolecular hydrogen bonding is mainly responsible for the three-dimensional ice lattice (see Figure 12.12). Other examples of molecular crystals are  $\text{I}_2$ ,  $\text{P}_4$ , and  $\text{S}_8$ .

In general, except in ice, molecules in molecular crystals are packed together as closely as their size and shape allow. Because van der Waals forces and hydrogen bonding are generally quite weak compared with covalent and ionic bonds, molecular crystals are more easily broken apart than ionic and covalent crystals. Indeed, most molecular crystals melt below  $200^\circ\text{C}$ .

## Covalent Crystals

In covalent crystals (sometimes called covalent network crystals), atoms are held together entirely by covalent bonds in an extensive three-dimensional network. No discrete molecules are present, as in the case of molecular solids. Well-known examples are the two allotropes of carbon: diamond and graphite (see Figure 8.14). In diamond each carbon atom is tetrahedrally bonded to four other atoms (Figure 12.22). The strong covalent bonds in three dimensions contribute to diamond's unusual hardness (it is the hardest material known) and high melting point ( $3550^\circ\text{C}$ ). In graphite, carbon atoms are arranged in six-membered rings. The atoms are all  $sp^2$ -hybridized; each atom is covalently bonded to three other atoms. The unhybridized  $2p$  orbital is used in pi bonding. In fact, the electrons in these  $2p$  orbitals are free to move around, making graphite a good conductor of electricity in the planes of the bonded carbon atoms. The layers are held together by the weak van der Waals forces. The covalent bonds in graphite account for its hardness; however, because the layers can slide over one another, graphite is slippery to the touch and is effective as a lubricant. It is also used in pencils and in ribbons made for computer printers and typewriters.

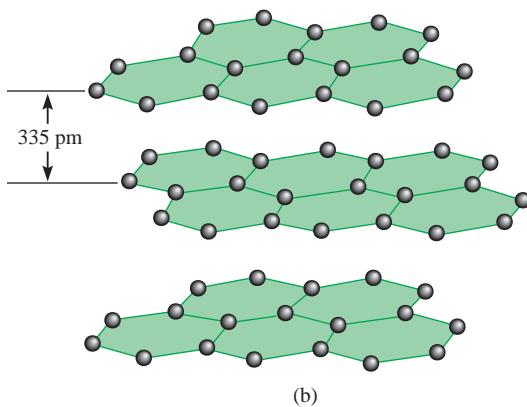
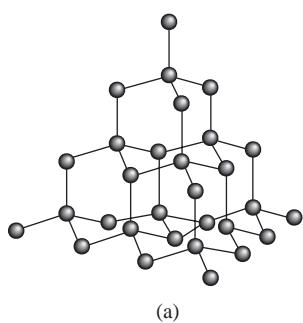


Sulfur.

**The central electrode in flashlight batteries is made of graphite.**

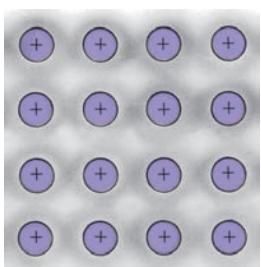
**Figure 12.22**

(a) The structure of diamond. Each carbon is tetrahedrally bonded to four other carbon atoms. (b) The structure of graphite. The distance between successive layers is 335 pm.



Quartz.

This comparison applies only to representative metals.

**Figure 12.23**

A cross section of a metallic crystal. Each circled positive charge represents the nucleus and inner electrons of a metal atom. The gray area surrounding the positive metal ions indicates the mobile sea of electrons.

Another type of covalent crystal is quartz ( $\text{SiO}_2$ ). The arrangement of silicon atoms in quartz is similar to that of carbon in diamond, but in quartz there is an oxygen atom between each pair of Si atoms. Because Si and O have different electronegativities (see Figure 9.4), the Si—O bond is polar. Nevertheless,  $\text{SiO}_2$  is similar to diamond in many respects, such as hardness and high melting point (1610°C).

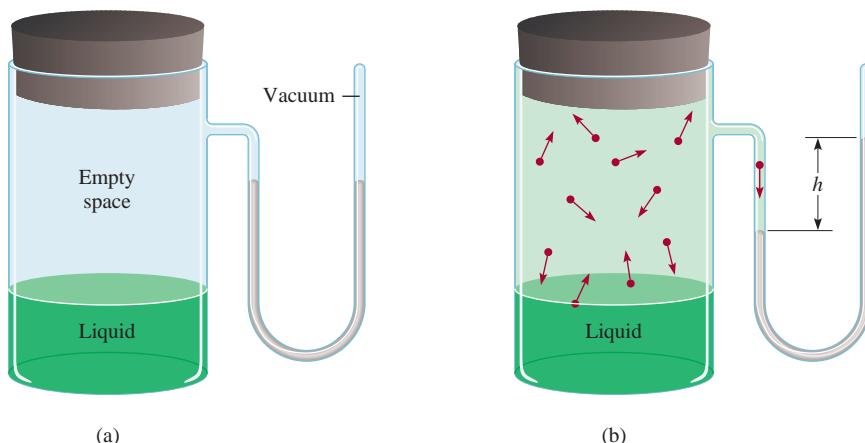
## Metallic Crystals

In a sense, the structure of metallic crystals is the simplest to deal with, because every lattice point in a crystal is occupied by an atom of the same metal. The bonding in metals is quite different from that in other types of crystals. In a metal, the bonding electrons are spread (or *delocalized*) over the entire crystal. In fact, metal atoms in a crystal can be imagined as an array of positive ions immersed in a sea of delocalized valence electrons (Figure 12.23). The great cohesive force resulting from delocalization is responsible for a metal's strength, which increases as the number of electrons available for bonding increases. For example, the melting point of sodium, with one valence electron, is 97.6°C, whereas that of aluminum, with three valence electrons, is 660°C. The mobility of the delocalized electrons makes metals good conductors of heat and electricity.

Solids are most stable in crystalline form. However, if a solid is formed rapidly (for example, when a liquid is cooled quickly), its atoms or molecules do not have time to align themselves and may become locked in positions other than those of a regular crystal. The resulting solid is said to be *amorphous*. **Amorphous solids**, such as glass, lack a regular three-dimensional arrangement of atoms.

## 12.6 Phase Changes

The discussions in Chapter 5 and in this chapter have given us an overview of the properties of the three states of matter: gas, liquid, and solid. Each of these states is often referred to as a **phase**, which is a homogeneous part of the system in contact with other parts of the system but separated from them by a well-defined boundary. An ice cube floating in water makes up two phases of water—the solid phase (ice) and the liquid phase (water). **Phase changes**, transformations from one phase to another, occur when energy (usually in the form of heat) is added or removed. Phase changes are physical changes that are characterized by changes in molecular order; molecules in the solid state have the most order, and those in the gas phase have the

**Figure 12.24**

Apparatus for measuring the vapor pressure of a liquid (a) before the evaporation begins and (b) at equilibrium, when no further change is evident. In (b) the number of molecules leaving the liquid is equal to the number of molecules returning to the liquid. The difference in the mercury levels ( $h$ ) gives the equilibrium vapor pressure of the liquid at the specified temperature.

greatest randomness. Keeping in mind the relationship between energy change and the increase or decrease in molecular order will help us understand the nature of phase changes.

## Liquid-Vapor Equilibrium

### Vapor Pressure

Molecules in a liquid are not fixed in a rigid lattice. Although they lack the total freedom of gaseous molecules, these molecules are in constant motion. Because liquids are denser than gases, the collision rate among molecules is much higher in the liquid phase than in the gas phase. *At any given temperature, a certain number of the molecules in a liquid possess sufficient kinetic energy to escape from the surface.* This process is called **evaporation**, or **vaporization**.

The difference between a gas and a vapor is explained on p. 133.

When a liquid evaporates, its gaseous molecules exert a vapor pressure. Consider the apparatus shown in Figure 12.24. Before the evaporation process starts, the mercury levels in the U-shaped manometer are equal. As soon as some molecules leave the liquid, a vapor phase is established. The vapor pressure is measurable only when a fair amount of vapor is present. The process of evaporation does not continue indefinitely, however. Eventually, the mercury levels stabilize and no further changes are seen.

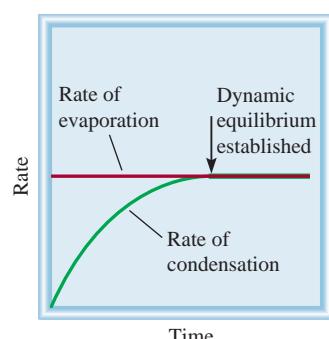
What happens at the molecular level during evaporation? In the beginning, the traffic is only one way: Molecules are moving from the liquid to the empty space. Soon the molecules in the space above the liquid establish a vapor phase. *As the concentration of molecules in the vapor phase increases, some molecules return to the liquid phase*, a process called **condensation**. Condensation occurs because a molecule striking the liquid surface becomes trapped by intermolecular forces in the liquid.

The rate of evaporation is constant at any given temperature, and the rate of condensation increases with increasing concentration of molecules in the vapor phase. A state of **dynamic equilibrium**, in which *the rate of a forward process is exactly balanced by the rate of the reverse process*, is reached when the rates of condensation and evaporation become equal (Figure 12.25). *The vapor pressure measured under dynamic equilibrium of condensation and evaporation is called the equilibrium vapor pressure.* We often use the simpler term “vapor pressure” when we talk about the equilibrium vapor pressure of a liquid. This practice is acceptable as long as we know the meaning of the abbreviated term.

It is important to note that the equilibrium vapor pressure is the *maximum vapor pressure* a liquid exerts at a given temperature and that it is constant at



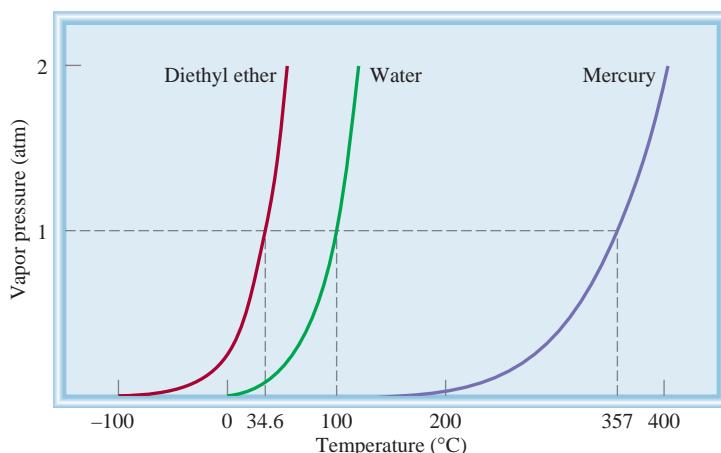
**Animation:**  
Equilibrium Vapor Pressure  
ARIS, Animations

**Figure 12.25**

Comparison of the rates of evaporation and condensation at constant temperature.

**Figure 12.26**

The increase in vapor pressure with temperature for three liquids. The normal boiling points of the liquids (at 1 atm) are shown on the horizontal axis.



**Equilibrium vapor pressure is independent of the amount of liquid as long as there is some liquid present.**

constant temperature. Vapor pressure does change with temperature, however. Plots of vapor pressure versus temperature for three different liquids are shown in Figure 12.26. We know that the number of molecules with higher kinetic energies is greater at the higher temperature and therefore so is the evaporation rate. For this reason, the vapor pressure of a liquid always increases with temperature. For example, the vapor pressure of water is 17.5 mmHg at 20°C, but it rises to 760 mmHg at 100°C.

### Heat of Vaporization and Boiling Point

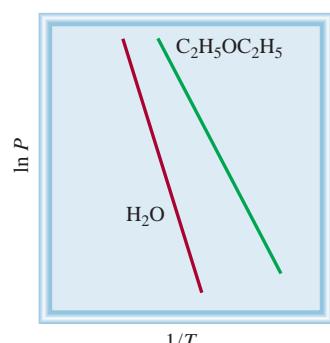
A measure of how strongly molecules are held in a liquid is its **molar heat of vaporization** ( $\Delta H_{\text{vap}}$ ), defined as the energy (usually in kilojoules) required to vaporize one mole of a liquid. The molar heat of vaporization is directly related to the strength of intermolecular forces that exist in the liquid. If the intermolecular attraction is strong, it takes a lot of energy to free the molecules from the liquid phase. Consequently, the liquid has a relatively low vapor pressure and a high molar heat of vaporization.

The quantitative relationship between the vapor pressure  $P$  of a liquid and the absolute temperature  $T$  is given by the Clausius-Clapeyron equation

$$\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + C \quad (12.1)$$

in which  $\ln$  is the natural logarithm,  $R$  is the gas constant (8.314 J/K · mol), and  $C$  is a constant. The Clausius-Clapeyron equation has the form of the linear equation  $y = mx + b$ :

$$\begin{aligned} \ln P &= \left( -\frac{\Delta H_{\text{vap}}}{R} \right) \left( \frac{1}{T} \right) + C \\ y &= m x + b \end{aligned}$$

**Figure 12.27**

Plots of  $\ln P$  versus  $1/T$  for water and diethyl ether. The slope in each case is equal to  $-\Delta H_{\text{vap}}/R$ .

By measuring the vapor pressure of a liquid at different temperatures and plotting  $\ln P$  versus  $1/T$ , we determine the slope of the line described by the equation, which is equal to  $-\Delta H_{\text{vap}}/R$ . ( $\Delta H_{\text{vap}}$  is assumed to be independent of temperature.) This is the method used to determine heats of vaporization. Figure 12.27 shows plots of  $\ln P$  versus  $1/T$  for water and diethyl ether ( $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ ). Note that the straight line for water has a steeper slope because water has a larger  $\Delta H_{\text{vap}}$  (Table 12.5).

**TABLE 12.5** Molar Heats of Vaporization for Selected Liquids

| Substance                         | Boiling Point* (°C) | $\Delta H_{\text{vap}}$ (kJ/mol) |
|-----------------------------------|---------------------|----------------------------------|
| Argon (Ar)                        | -186                | 6.3                              |
| Benzene ( $C_6H_6$ )              | 80.1                | 31.0                             |
| Diethyl ether ( $C_2H_5OC_2H_5$ ) | 34.6                | 26.0                             |
| Ethanol ( $C_2H_5OH$ )            | 78.3                | 39.3                             |
| Mercury (Hg)                      | 357                 | 59.0                             |
| Methane ( $CH_4$ )                | -164                | 9.2                              |
| Water ( $H_2O$ )                  | 100                 | 40.79                            |

\*Measured at 1 atm.

If we know the values of  $\Delta H_{\text{vap}}$  and  $P$  of a liquid at one temperature, we can use the Clausius-Clapeyron equation to calculate the vapor pressure of the liquid at a different temperature. At temperatures  $T_1$  and  $T_2$  the vapor pressures are  $P_1$  and  $P_2$ . From Equation (12.1) we can write

$$\ln P_1 = -\frac{\Delta H_{\text{vap}}}{RT_1} + C \quad (12.2)$$

$$\ln P_2 = -\frac{\Delta H_{\text{vap}}}{RT_2} + C \quad (12.3)$$

Subtracting Equation (12.3) from Equation (12.2) we obtain

$$\begin{aligned} \ln P_1 - \ln P_2 &= -\frac{\Delta H_{\text{vap}}}{RT_1} - \left( -\frac{\Delta H_{\text{vap}}}{RT_2} \right) \\ &= \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \end{aligned}$$

Hence,

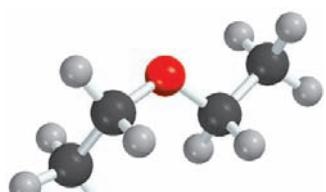
$$\begin{aligned} \ln \frac{P_1}{P_2} &= \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \\ \text{or } \ln \frac{P_1}{P_2} &= \frac{\Delta H_{\text{vap}}}{R} \left( \frac{T_1 - T_2}{T_1 T_2} \right) \end{aligned} \quad (12.4)$$

### Example 12.5

Diethyl ether is a volatile, highly flammable organic liquid that is used mainly as a solvent. The vapor pressure of diethyl ether is 401 mmHg at 18°C. Calculate its vapor pressure at 32°C.

**Strategy** We are given the vapor pressure of diethyl ether at one temperature and asked to find the pressure at another temperature. Therefore, we need Equation (12.4).

(Continued)



**Solution** Table 12.5 tells us that  $\Delta H_{\text{vap}} = 26.0 \text{ kJ/mol}$ . The data are

$$\begin{array}{ll} P_1 = 401 \text{ mmHg} & P_2 = ? \\ T_1 = 18^\circ\text{C} = 291 \text{ K} & T_2 = 32^\circ\text{C} = 305 \text{ K} \end{array}$$

From Equation (12.4) we have

$$\begin{aligned} \ln \frac{401}{P_2} &= \frac{26,000 \text{ J/mol}}{8.314 \text{ J/K} \cdot \text{mol}} \left[ \frac{291 \text{ K} - 305 \text{ K}}{(291 \text{ K})(305 \text{ K})} \right] \\ &= -0.493 \end{aligned}$$

Taking the antilog of both sides (see Appendix 3), we obtain

$$\frac{401}{P_2} = e^{-0.493} = 0.611$$

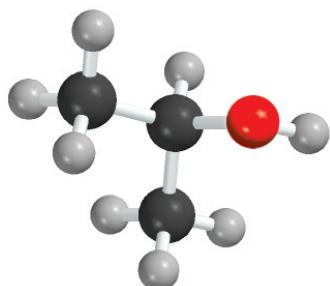
Hence,

$$P_2 = 656 \text{ mmHg}$$

**Similar problem:** 12.80.

**Check** We expect the vapor pressure to be greater at the higher temperature. Therefore, the answer is reasonable.

**Practice Exercise** The vapor pressure of ethanol is 100 mmHg at 34.9°C. What is its vapor pressure at 63.5°C? ( $\Delta H_{\text{vap}}$  for ethanol is 39.3 kJ/mol.)



Isopropanol (rubbing alcohol)

A practical way to demonstrate the molar heat of vaporization is by rubbing alcohol on your hands. The heat from your hands increases the kinetic energy of the alcohol molecules. The alcohol evaporates rapidly, extracting heat from your hands and cooling them. The process is similar to perspiration, which is one means by which the human body maintains a constant temperature. Because of the strong intermolecular hydrogen bonding that exists in water, a considerable amount of energy is needed to vaporize the water in perspiration from the body's surface. This energy is supplied by the heat generated in various metabolic processes.

You have already seen that the vapor pressure of a liquid increases with temperature. For every liquid there exists a temperature at which the liquid begins to boil. The **boiling point** is the temperature at which the vapor pressure of a liquid is equal to the external pressure. The normal boiling point of a liquid is the boiling point when the external pressure is 1 atm.

At the boiling point, bubbles form within the liquid. When a bubble forms, the liquid originally occupying that space is pushed aside, and the level of the liquid in the container is forced to rise. The pressure exerted on the bubble is largely atmospheric pressure, plus some *hydrostatic pressure* (that is, pressure caused by the presence of liquid). The pressure inside the bubble is due solely to the vapor pressure of the liquid. When the vapor pressure equals the external pressure, the bubble rises to the surface of the liquid and bursts. If the vapor pressure in the bubble were lower than the external pressure, the bubble would collapse before it could rise. We can thus conclude that the boiling point of a liquid depends on the external pressure. (We usually ignore the small contribution caused by the hydrostatic pressure.) For example, at 1 atm water boils at 100°C, but if the pressure is reduced to 0.5 atm, water boils at only 82°C.

Because the boiling point is defined in terms of the vapor pressure of the liquid, we expect the boiling point to be related to the molar heat of vaporization: The higher

$\Delta H_{\text{vap}}$ , the higher the boiling point. The data in Table 12.5 roughly confirm our prediction. Ultimately, both the boiling point and  $\Delta H_{\text{vap}}$  are determined by the strength of intermolecular forces. For example, argon (Ar) and methane ( $\text{CH}_4$ ), which have weak dispersion forces, have low boiling points and small molar heats of vaporization. Diethyl ether ( $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ ) has a dipole moment, and the dipole-dipole forces account for its moderately high boiling point and  $\Delta H_{\text{vap}}$ . Both ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) and water have strong hydrogen bonding, which accounts for their high boiling points and large  $\Delta H_{\text{vap}}$  values. Strong metallic bonding causes mercury to have the highest boiling point and  $\Delta H_{\text{vap}}$  of this group of liquids. Interestingly, the boiling point of benzene, which is nonpolar, is comparable to that of ethanol. Benzene has a large polarizability, and the dispersion forces among benzene molecules can be as strong as or even stronger than dipole-dipole forces and/or hydrogen bonds.

### Critical Temperature and Pressure

The opposite of evaporation is condensation. In principle, a gas can be made to liquefy by either one of two techniques. By cooling a sample of gas we decrease the kinetic energy of its molecules, and eventually molecules aggregate to form small drops of liquid. Alternatively, we may apply pressure to the gas. Under compression, the average distance between molecules is reduced so that they are held together by mutual attraction. Industrial liquefaction processes combine these two methods.

Every substance has a **critical temperature** ( $T_c$ ), above which its gas form cannot be made to liquefy, no matter how great the applied pressure. This is also the highest temperature at which a substance can exist as a liquid. The minimum pressure that must be applied to bring about liquefaction at the critical temperature is called the **critical pressure** ( $P_c$ ). The existence of the critical temperature can be qualitatively explained as follows. The intermolecular attraction is a finite quantity for any given substance. Below  $T_c$ , this force is sufficiently strong to hold the molecules together (under some appropriate pressure) in a liquid. Above  $T_c$ , molecular motion becomes so energetic that the molecules can always break away from this attraction. Figure 12.28 shows what happens when sulfur hexafluoride is heated above its critical temperature ( $45.5^\circ\text{C}$ ) and then cooled down to below  $45.5^\circ\text{C}$ .

Table 12.6 lists the critical temperatures and critical pressures of a number of common substances. Benzene, ethanol, mercury, and water, which have strong intermolecular forces, also have high critical temperatures compared with the other substances listed in the table.

Intermolecular forces are independent of temperature; the kinetic energy of molecules increases with temperature.

### Liquid-Solid Equilibrium

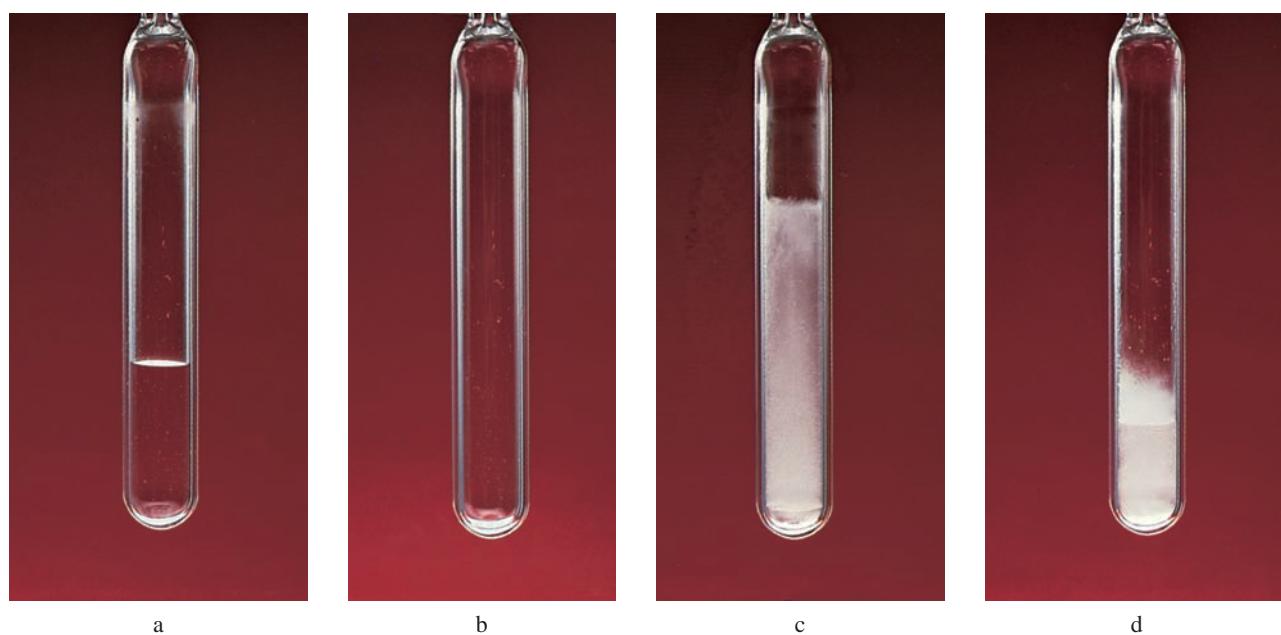
The transformation of liquid to solid is called *freezing*, and the reverse process is called *melting* or *fusion*. The **melting point** of a solid (or the freezing point of a liquid) is the temperature at which solid and liquid phases coexist in equilibrium. The *normal* melting point (or the *normal* freezing point) of a substance is the melting point (or freezing point) measured at 1 atm pressure. We generally omit the word “normal” in referring to the melting point of a substance at 1 atm.

“Fusion” refers to the process of melting. Thus, a “fuse” breaks an electrical circuit when a metallic strip melts due to the heat generated by excessively high electrical current.

The most familiar liquid-solid equilibrium is that of water and ice. At  $0^\circ\text{C}$  and 1 atm, the dynamic equilibrium is represented by



A practical illustration of this dynamic equilibrium is provided by a glass of ice water. As the ice cubes melt to form water, some of the water between the ice cubes may

**Figure 12.28**

The critical phenomenon of sulfur hexafluoride. (a) Below the critical temperature the clear liquid phase is visible. (b) Above the critical temperature the liquid phase has disappeared. (c) The substance is cooled just below its critical temperature. The fog represents the condensation of vapor. (d) Finally, the liquid phase reappears.

freeze, thus joining the cubes together. This is not a true dynamic equilibrium; because the glass is not kept at 0°C, all the ice cubes will eventually melt away.

The energy (usually in kilojoules) required to melt 1 mole of a solid is called the **molar heat of fusion ( $\Delta H_{fus}$ )**. Table 12.7 shows the molar heats of fusion for the substances listed in Table 12.5. A comparison of the data in the two tables shows that for each substance  $\Delta H_{fus}$  is smaller than  $\Delta H_{vap}$ . This is consistent with the fact that

**TABLE 12.6 Critical Temperatures and Critical Pressures of Selected Substances**

| Substance   | $T_c$ (°C) | $P_c$ (atm) |
|---|------------|-------------|
| Ammonia (NH <sub>3</sub> )  | 132.4      | 111.5       |
| Argon (Ar)  | -186       | 6.3         |
| Benzene (C <sub>6</sub> H <sub>6</sub> )                                      | 288.9      | 47.9        |
| Carbon dioxide (CO <sub>2</sub> )   | 31.0       | 73.0        |
| Diethyl ether (C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub> ) | 192.6      | 35.6        |
| Ethanol (C <sub>2</sub> H <sub>5</sub> OH)                                    | 243        | 63.0        |
| Mercury (Hg)  | 1462       | 1036        |
| Methane (CH <sub>4</sub> )  | -83.0      | 45.6        |
| Molecular hydrogen (H <sub>2</sub> )  | -239.9     | 12.8        |
| Molecular nitrogen (N <sub>2</sub> )  | -147.1     | 33.5        |
| Molecular oxygen (O <sub>2</sub> )  | -118.8     | 49.7        |
| Sulfur hexafluoride (SF <sub>6</sub> )  | 45.5       | 37.6        |
| Water (H <sub>2</sub> O)  | 374.4      | 219.5       |

**TABLE 12.7 Molar Heats of Fusion for Selected Substances**

| Substance                         | Melting Point* (°C) | $\Delta H_{\text{fus}}$ (kJ/mol) |
|-----------------------------------|---------------------|----------------------------------|
| Argon (Ar)                        | -190                | 1.3                              |
| Benzene ( $C_6H_6$ )              | 5.5                 | 10.9                             |
| Diethyl ether ( $C_2H_5OC_2H_5$ ) | -116.2              | 6.90                             |
| Ethanol ( $C_2H_5OH$ )            | -117.3              | 7.61                             |
| Mercury (Hg)                      | -39                 | 23.4                             |
| Methane ( $CH_4$ )                | -183                | 0.84                             |
| Water ( $H_2O$ )                  | 0                   | 6.01                             |

\*Measured at 1 atm.

molecules in a liquid are fairly closely packed together, so that some energy is needed to bring about the rearrangement from solid to liquid. On the other hand, when a liquid evaporates, its molecules are completely separated from one another and considerably more energy is required to overcome the attractive forces.

## Solid-Vapor Equilibrium

Solids, too, undergo evaporation and therefore possess a vapor pressure. Consider the following dynamic equilibrium:



The process in which molecules go directly from the solid into the vapor phase is called **sublimation**, and the reverse process (that is, from vapor directly to solid) is called **deposition**. Naphthalene (the substance used to make mothballs) has a fairly high vapor pressure for a solid (1 mmHg at 53°C); thus its pungent vapor quickly permeates an enclosed space. Generally, because molecules are more tightly held in a solid, the vapor pressure of a solid is much less than that of the corresponding liquid. The energy (usually in kilojoules) required to sublime 1 mole of a solid, called the **molar heat of sublimation** ( $\Delta H_{\text{sub}}$ ), is given by the sum of the molar heats of fusion and vaporization:

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}} \quad (12.5)$$

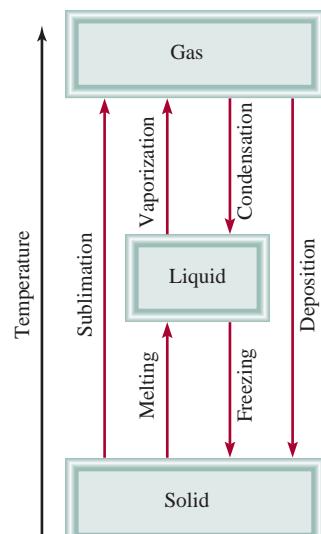
Strictly speaking, Equation (12.5), which is an illustration of Hess's law, holds if all the phase changes occur at the same temperature. The enthalpy, or heat change, for the overall process is the same whether the substance changes directly from the solid to the vapor form or goes from solid to liquid and then to vapor. Figure 12.29 summarizes the types of phase changes discussed in this section.

## 12.7 Phase Diagrams

The overall relationships among the solid, liquid, and vapor phases are best represented in a single graph known as a phase diagram. A **phase diagram** summarizes the conditions under which a substance exists as a solid, liquid, or gas. In this section we will briefly discuss the phase diagrams of water and carbon dioxide.

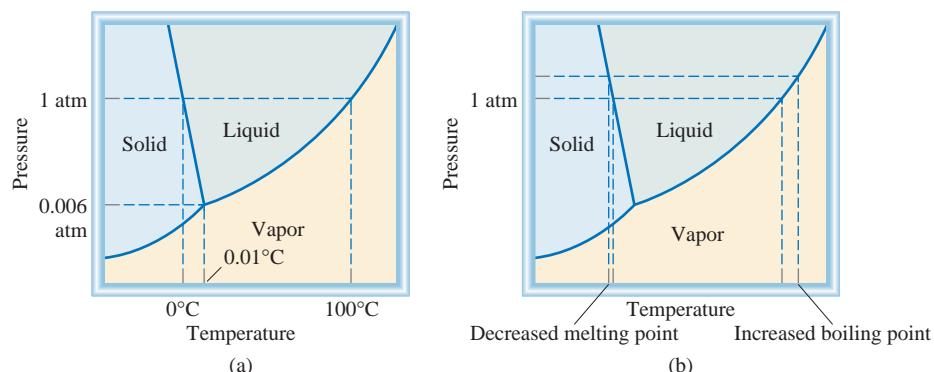


Solid iodine in equilibrium with its vapor.

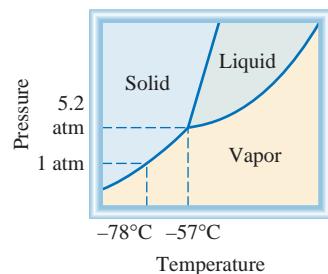


**Figure 12.29**

The various phase changes that a substance can undergo.

**Figure 12.30**

(a) The phase diagram of water. Each solid line between two phases specifies the conditions of pressure and temperature under which the two phases can exist in equilibrium. The point at which all three phases can exist in equilibrium (0.006 atm and 0.01°C) is called the triple point. (b) This phase diagram tells us that increasing the pressure on ice lowers its melting point and that increasing the pressure of liquid water raises its boiling point.

**Figure 12.31**

The phase diagram of carbon dioxide. Note that the solid-liquid boundary line has a positive slope. The liquid phase is not stable below 5.2 atm, so that only the solid and vapor phases can exist under atmospheric conditions.

**Figure 12.32**

Under atmospheric conditions, solid carbon dioxide does not melt; it can only sublime. The cold carbon dioxide gas causes nearby water vapor to condense and form a fog.

## Water

Figure 12.30(a) shows the phase diagram of water. The graph is divided into three regions, each of which represents a pure phase. The line separating any two regions indicates conditions under which these two phases can exist in equilibrium. For example, the curve between the liquid and vapor phases shows the variation of vapor pressure with temperature. The other two curves similarly indicate conditions for equilibrium between ice and liquid water and between ice and water vapor. (Note that the solid-liquid boundary line has a negative slope.) The point at which all three curves meet is called the **triple point**. For water, this point is at 0.01°C and 0.006 atm. This is *the only temperature and pressure at which all three phases can be in equilibrium with one another*.

Phase diagrams enable us to predict changes in the melting point and boiling point of a substance as a result of changes in the external pressure; we can also anticipate directions of phase transitions brought about by changes in temperature and pressure. The normal melting point and boiling point of water, measured at 1 atm, are 0°C and 100°C, respectively. What would happen if melting and boiling were carried out at some other pressure? Figure 12.30(b) shows clearly that increasing the pressure above 1 atm will raise the boiling point and lower the melting point. A decrease in pressure will lower the boiling point and raise the melting point.

## Carbon Dioxide

The phase diagram of carbon dioxide (Figure 12.31) is similar to that of water, with one important exception—the slope of the curve between solid and liquid is positive. In fact, this holds true for almost all other substances. Water behaves differently because ice is less dense than liquid water. The triple point of carbon dioxide is at 5.2 atm and -57°C.

An interesting observation can be made about the phase diagram in Figure 12.31. As you can see, the entire liquid phase lies well above atmospheric pressure; therefore, it is impossible for solid carbon dioxide to melt at 1 atm. Instead, when solid CO<sub>2</sub> is heated to -78°C at 1 atm, it sublimes. In fact, solid carbon dioxide is called dry ice because it looks like ice and *does not melt* (Figure 12.32). Because of this property, dry ice is useful as a refrigerant.

## KEY EQUATIONS

$$\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + C \quad (12.1)$$

Clausius-Clapeyron equation for determining  $\Delta H_{\text{vap}}$  of a liquid.

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{T_1 - T_2}{T_1 T_2} \right) \quad (12.4)$$

For calculating  $\Delta H_{\text{vap}}$ , vapor pressure, or boiling point of a liquid.

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}} \quad (12.5)$$

Application of Hess's law.

## SUMMARY OF FACTS AND CONCEPTS

- All substances exist in one of three states: gas, liquid, or solid. The major difference between the condensed states and the gaseous state is the distance of separation between molecules.
- Intermolecular forces act between molecules or between molecules and ions. Generally, these forces are much weaker than bonding forces. Dipole-dipole forces and ion-dipole forces attract molecules with dipole moments to other polar molecules or ions. Dispersion forces are the result of temporary dipole moments induced in ordinarily nonpolar molecules. The extent to which a dipole moment can be induced in a molecule is determined by its polarizability. The term “van der Waals forces” refers to dipole-dipole, dipole-induced dipole, and dispersion forces.
- Hydrogen bonding is a relatively strong dipole-dipole force that acts between a polar bond containing a hydrogen atom and the bonded electronegative atoms, N, O, or F. Hydrogen bonds between water molecules are particularly strong.
- Liquids tend to assume a geometry that ensures the minimum surface area. Surface tension is the energy needed to expand a liquid surface area; strong intermolecular forces lead to greater surface tension. Viscosity is a measure of the resistance of a liquid to flow; it decreases with increasing temperature.
- Water molecules in the solid state form a three-dimensional network in which each oxygen atom is covalently bonded to two hydrogen atoms and is hydrogen-bonded to two hydrogen atoms. This unique structure accounts for the fact that ice is less dense than liquid water. Water is also ideally suited for its ecological role by its high specific heat, another property imparted by its strong hydrogen bonding. Large bodies of water are able to moderate the climate by giving off and absorbing substantial amounts of heat with only small changes in the water temperature.
- All solids are either crystalline (with a regular structure of atoms, ions, or molecules) or amorphous (without a regular structure). The basic structural unit of a crystalline solid is the unit cell, which is repeated to form a three-dimensional crystal lattice.
- The four types of crystals and the forces that hold their particles together are ionic crystals, held together by ionic bonding; molecular crystals, van der Waals forces and/or hydrogen bonding; covalent crystals, covalent bonding; and metallic crystals, metallic bonding.
- A liquid in a closed vessel eventually establishes a dynamic equilibrium between evaporation and condensation. The vapor pressure over the liquid under these conditions is the equilibrium vapor pressure, which is often referred to simply as vapor pressure. At the boiling point, the vapor pressure of a liquid equals the external pressure. The molar heat of vaporization of a liquid is the energy required to vaporize 1 mole of the liquid. It can be determined by measuring the vapor pressure of the liquid as a function of temperature and using Equation (12.1). The molar heat of fusion of a solid is the energy required to melt 1 mole of the solid.
- For every substance there is a temperature, called the critical temperature, above which its gas form cannot be made to liquefy.
- The relationships among the three phases of a single substance are represented by a phase diagram, in which each region represents a pure phase and the boundaries between the regions show the temperatures and pressures at which the two phases are in equilibrium. At the triple point, all three phases are in equilibrium.

## KEY WORDS

|  |                                    |  |                              |
|--|------------------------------------|--|------------------------------|
| Adhesion, p. 398                       | Dipole-dipole forces, p. 392       | Ion-dipole forces, p. 392                                      | Phase changes, p. 408        |
| Amorphous solid, p. 408                | Dispersion forces, p. 394          | Lattice point, p. 401  | Phase diagram, p. 415        |
| Boiling point, p. 412                  | Dynamic equilibrium, p. 409        | Melting point, p. 413  | Polarizability, p. 393       |
| Cohesion, p. 398                       | Equilibrium vapor pressure, p. 409 | Molar heat of fusion ( $\Delta H_{\text{fus}}$ ), p. 414       | Sublimation, p. 415          |
| Condensation, p. 409                   | Evaporation, p. 409                | Molar heat of sublimation ( $\Delta H_{\text{sub}}$ ), p. 415  | Surface tension, p. 398      |
| Coordination number, p. 403            | Hydrogen bond, p. 396              | Molar heat of vaporization ( $\Delta H_{\text{vap}}$ ), p. 410 | Triple point, p. 416         |
| Critical pressure ( $P_c$ ), p. 413    | Induced dipole, p. 393             | Phase, p. 408  | Unit cell, p. 401            |
| Critical temperature ( $T_c$ ), p. 413 | Intermolecular forces, p. 392      |  | van der Waals forces, p. 392 |
| Crystalline solid, p. 401              | Intramolecular forces, p. 392      |  | Vaporization, p. 409         |
| Deposition, p. 415                     |                                    |  | Viscosity, p. 398            |

## QUESTIONS AND PROBLEMS

### Intermolecular Forces

#### Review Questions

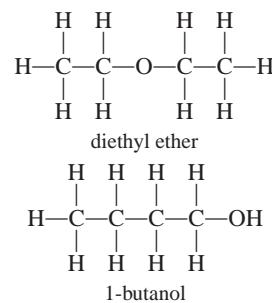
- 12.1 Define these terms and give an example for each category: (a) dipole-dipole interaction, (b) dipole-induced dipole interaction, (c) ion-dipole interaction, (d) dispersion forces, (e) van der Waals forces.
- 12.2 Explain the term “polarizability.” What kind of molecules tend to have high polarizabilities? What is the relationship between polarizability and intermolecular forces?
- 12.3 Explain the difference between the temporary dipole moment induced in a molecule and the permanent dipole moment in a polar molecule.
- 12.4 Give some evidence that all molecules exert attractive forces on one another.
- 12.5 What type of physical properties would you need to consider in comparing the strength of intermolecular forces in solids and in liquids?
- 12.6 Which elements can take part in hydrogen bonding?

#### Problems

- 12.7 The compounds  $\text{Br}_2$  and  $\text{ICl}$  have the same number of electrons, yet  $\text{Br}_2$  melts at  $-7.2^\circ\text{C}$ , whereas  $\text{ICl}$  melts at  $27.2^\circ\text{C}$ . Explain.
- 12.8 If you lived in Alaska, state which of these natural gases you would keep in an outdoor storage tank in winter and explain why: methane ( $\text{CH}_4$ ), propane ( $\text{C}_3\text{H}_8$ ), or butane ( $\text{C}_4\text{H}_{10}$ ).
- 12.9 The binary hydrogen compounds of the Group 4A elements are  $\text{CH}_4$  ( $-162^\circ\text{C}$ ),  $\text{SiH}_4$  ( $-112^\circ\text{C}$ ),  $\text{GeH}_4$  ( $-88^\circ\text{C}$ ), and  $\text{SnH}_4$  ( $-52^\circ\text{C}$ ). The temperatures in

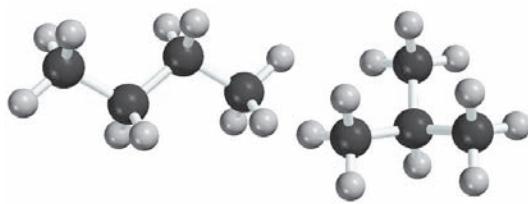
(b) parentheses are the corresponding boiling points. Explain the increase in boiling points from  $\text{CH}_4$  to  $\text{SnH}_4$ .

- 12.10 List the types of intermolecular forces that exist in each of these species: (a) benzene ( $\text{C}_6\text{H}_6$ ), (b)  $\text{CH}_3\text{Cl}$ , (c)  $\text{PF}_3$ , (d)  $\text{NaCl}$ , (e)  $\text{CS}_2$ .
- 12.11 Ammonia is both a donor and an acceptor of hydrogen in hydrogen bond formation. Draw a diagram to show the hydrogen bonding of an ammonia molecule with two other ammonia molecules.
- 12.12 Which of these species are capable of hydrogen bonding among themselves: (a)  $\text{C}_2\text{H}_6$ , (b)  $\text{HI}$ , (c)  $\text{KF}$ , (d)  $\text{BeH}_2$ , (e)  $\text{CH}_3\text{COOH}$ ?
- 12.13 Arrange the following compounds in order of increasing boiling point:  $\text{RbF}$ ,  $\text{CO}_2$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{Br}$ . Explain your arrangement.
- 12.14 Diethyl ether has a boiling point of  $34.5^\circ\text{C}$ , and 1-butanol has a boiling point of  $117^\circ\text{C}$ .



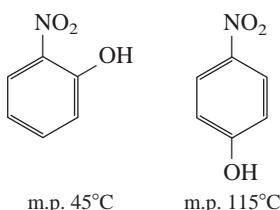
Both of these compounds have the same numbers and types of atoms. Explain the difference in their boiling points.

- 12.15 Which member of each of these pairs of substances would you expect to have a higher boiling point: (a) O<sub>2</sub> or N<sub>2</sub>, (b) SO<sub>2</sub> or CO<sub>2</sub>, (c) HF or HI?
- 12.16** State which substance in each of these pairs you would expect to have the higher boiling point and explain why: (a) Ne or Xe, (b) CO<sub>2</sub> or CS<sub>2</sub>, (c) CH<sub>4</sub> or Cl<sub>2</sub>, (d) F<sub>2</sub> or LiF, (e) NH<sub>3</sub> or PH<sub>3</sub>.
- 12.17 Explain in terms of intermolecular forces why (a) NH<sub>3</sub> has a higher boiling point than CH<sub>4</sub> and (b) KCl has a higher melting point than I<sub>2</sub>.
- 12.18** What kind of attractive forces must be overcome to (a) melt ice, (b) boil molecular bromine, (c) melt solid iodine, and (d) dissociate F<sub>2</sub> into F atoms?
- 12.19 These nonpolar molecules have the same number and type of atoms. Which one would you expect to have a higher boiling point?



(Hint: Molecules that can be stacked together more easily have greater intermolecular attraction.)

- 12.20** Explain the difference in the melting points of these compounds:



(Hint: Only one of the two can form intramolecular hydrogen bonds.)

## The Liquid State

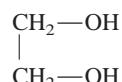
### Review Questions

- 12.21 Explain why liquids, unlike gases, are virtually incompressible.
- 12.22 Define surface tension. What is the relationship between the intermolecular forces that exist in a liquid and its surface tension?
- 12.23 Despite the fact that stainless steel is much denser than water, a stainless-steel razor blade can be made to float on water. Why?

- 12.24 Use water and mercury as examples to explain adhesion and cohesion.
- 12.25 A glass can be filled slightly above the rim with water. Explain why the water does not overflow.
- 12.26 Draw diagrams showing the capillary action of (a) water and (b) mercury in three tubes of different radii.
- 12.27 What is viscosity? What is the relationship between the intermolecular forces that exist in a liquid and its viscosity?
- 12.28 Why does the viscosity of a liquid decrease with increasing temperature?
- 12.29 Why is ice less dense than water?
- 12.30 Outdoor water pipes have to be drained or insulated in winter in a cold climate. Why?

### Problems

- 12.31 Predict which of these liquids has the greater surface tension: ethanol (C<sub>2</sub>H<sub>5</sub>OH) or dimethyl ether (CH<sub>3</sub>OCH<sub>3</sub>).
- 12.32** Predict the viscosity of ethylene glycol



relative to that of ethanol and glycerol (see Table 12.3).

## Crystalline Solids

### Review Questions

- 12.33 Define these terms: crystalline solid, lattice point, unit cell, coordination number.
- 12.34 Describe the geometries of these cubic cells: simple cubic cell, body-centered cubic cell, face-centered cubic cell. Which of these cells would give the highest density for the same type of atoms?

### Problems

- 12.35 Describe, with examples, these types of crystals: (a) ionic crystals, (b) covalent crystals, (c) molecular crystals, (d) metallic crystals.
- 12.36** A solid is hard, brittle, and electrically nonconducting. Its melt (the liquid form of the substance) and an aqueous solution containing the substance do conduct electricity. Classify the solid.
- 12.37 A solid is soft and has a low melting point (below 100°C). The solid, its melt, and a solution containing the substance are all nonconductors of electricity. Classify the solid.
- 12.38** A solid is very hard and has a high melting point. Neither the solid nor its melt conducts electricity. Classify the solid.

- 12.39 Why are metals good conductors of heat and electricity? Why does the ability of a metal to conduct electricity decrease with increasing temperature?
- 12.40** Classify the solid states of the elements in the second period of the periodic table.
- 12.41 The melting points of the oxides of the third-period elements are given in parentheses:  $\text{Na}_2\text{O}$  (1275°C),  $\text{MgO}$  (2800°C),  $\text{Al}_2\text{O}_3$  (2045°C),  $\text{SiO}_2$  (1610°C),  $\text{P}_4\text{O}_{10}$  (580°C),  $\text{SO}_3$  (16.8°C),  $\text{Cl}_2\text{O}_7$  (-91.5°C). Classify these solids.
- 12.42** Which of these are molecular solids and which are covalent solids:  $\text{Se}_8$ ,  $\text{HBr}$ ,  $\text{Si}$ ,  $\text{CO}_2$ ,  $\text{C}$ ,  $\text{P}_4\text{O}_6$ ,  $\text{B}$ ,  $\text{SiH}_4$ ?
- 12.43 What is the coordination number of each sphere in (a) a simple cubic lattice, (b) a body-centered cubic lattice, and (c) a face-centered cubic lattice? Assume the spheres to be of equal size.
- 12.44** Calculate the number of spheres in these unit cells: simple cubic, body-centered cubic, and face-centered cubic cells. Assume that the spheres are of equal size and that they are only at the lattice points.
- 12.45 Metallic iron crystallizes in a cubic lattice. The unit cell edge length is 287 pm. The density of iron is 7.87 g/cm<sup>3</sup>. How many iron atoms are there within a unit cell?
- 12.46** Barium metal crystallizes in a body-centered cubic lattice (the Ba atoms are at the lattice points only). The unit cell edge length is 502 pm, and the density of Ba is 3.50 g/cm<sup>3</sup>. Using this information, calculate Avogadro's number. (*Hint:* First calculate the volume occupied by 1 mole of Ba atoms in the unit cells. Next calculate the volume occupied by one of the Ba atoms in the unit cell.)
- 12.47 Vanadium crystallizes in a body-centered cubic lattice (the V atoms occupy only the lattice points). How many V atoms are in a unit cell?
- 12.48** Europium crystallizes in a body-centered cubic lattice (the Eu atoms occupy only the lattice points). The density of Eu is 5.26 g/cm<sup>3</sup>. Calculate the unit cell edge length in picometers.
- 12.49 Crystalline silicon has a cubic structure. The unit cell edge length is 543 pm. The density of the solid is 2.33 g/cm<sup>3</sup>. Calculate the number of Si atoms in one unit cell.
- 12.50** A face-centered cubic cell contains 8 X atoms at the corners of the cell and 6 Y atoms at the faces. What is the empirical formula of the solid?
- 12.51 Classify the crystalline form of these substances as ionic crystals, covalent crystals, molecular crystals, or metallic crystals: (a)  $\text{CO}_2$ , (b)  $\text{B}$ , (c)  $\text{S}_8$ , (d)  $\text{KBr}$ , (e)  $\text{Mg}$ , (f)  $\text{SiO}_2$ , (g)  $\text{LiCl}$ , (h)  $\text{Cr}$ .
- 12.52** Explain why diamond is harder than graphite. Why is graphite an electrical conductor but diamond is not?

## Phase Changes

### Review Questions

- 12.53 Define phase change. Name all possible changes that can occur among the vapor, liquid, and solid states of a substance.
- 12.54 What is the equilibrium vapor pressure of a liquid? How does it change with temperature?
- 12.55 Use any one of the phase changes to explain what is meant by dynamic equilibrium.
- 12.56 Define these terms: (a) molar heat of vaporization, (b) molar heat of fusion, (c) molar heat of sublimation. What are their units?
- 12.57 How is the molar heat of sublimation related to the molar heats of vaporization and fusion? On what law is this relation based?
- 12.58 What can we learn about the strength of intermolecular forces in a liquid from its molar heat of vaporization?
- 12.59 The greater the molar heat of vaporization of a liquid, the greater its vapor pressure. True or false?
- 12.60 Define boiling point. How does the boiling point of a liquid depend on external pressure? Referring to Table 5.2, what is the boiling point of water when the external pressure is 187.5 mmHg?
- 12.61 As a liquid is heated at constant pressure, its temperature rises. This trend continues until the boiling point of the liquid is reached. No further rise in the temperature of the liquid can be induced by heating. Explain.
- 12.62 Define critical temperature. What is the significance of critical temperature in the liquefaction of gases?
- 12.63 What is the relationship between intermolecular forces in a liquid and the liquid's boiling point and critical temperature? Why is the critical temperature of water greater than that of most other substances?
- 12.64 How do the boiling points and melting points of water and carbon tetrachloride vary with pressure? Explain any difference in behavior of these two substances.
- 12.65 Why is solid carbon dioxide called dry ice?
- 12.66 The vapor pressure of a liquid in a closed container depends on which of these: (a) the volume above the liquid, (b) the amount of liquid present, (c) temperature?
- 12.67 Referring to Figure 12.26, estimate the boiling points of diethyl ether, water, and mercury at 0.5 atm.
- 12.68 Wet clothes dry more quickly on a hot, dry day than on a hot, humid day. Explain.
- 12.69 Which of the following phase transitions gives off more heat: (a) 1 mole of steam to 1 mole of water at 100°C or (b) 1 mole of water to 1 mole of ice at 0°C?

- 12.70 A beaker of water is heated to boiling by a Bunsen burner. Would adding another burner raise the boiling point of water? Explain.

### Problems

- 12.71 Calculate the amount of heat (in kilojoules) required to convert 74.6 g of water to steam at 100°C.

- 12.72** How much heat (in kilojoules) is needed to convert 866 g of ice at  $-10^{\circ}\text{C}$  to steam at  $126^{\circ}\text{C}$ ? (The specific heats of ice and steam are  $2.03 \text{ J/g} \cdot ^{\circ}\text{C}$  and  $1.99 \text{ J/g} \cdot ^{\circ}\text{C}$ , respectively.)

- 12.73 How is the rate of evaporation of a liquid affected by (a) temperature, (b) the surface area of liquid exposed to air, (c) intermolecular forces?

- 12.74** The molar heats of fusion and sublimation of molecular iodine are 15.27 kJ/mol and 62.30 kJ/mol, respectively. Estimate the molar heat of vaporization of liquid iodine.

- 12.75 These compounds are liquid at  $-10^{\circ}\text{C}$ ; their boiling points are given: butane,  $-0.5^{\circ}\text{C}$ ; ethanol,  $78.3^{\circ}\text{C}$ ; toluene,  $110.6^{\circ}\text{C}$ . At  $-10^{\circ}\text{C}$ , which of these liquids would you expect to have the highest vapor pressure? Which the lowest?

- 12.76** Freeze-dried coffee is prepared by freezing a sample of brewed coffee and then removing the ice component by vacuum-pumping the sample. Describe the phase changes taking place during these processes.

- 12.77 A student hangs wet clothes outdoors on a winter day when the temperature is  $-15^{\circ}\text{C}$ . After a few hours, the clothes are found to be fairly dry. Describe the phase changes in this drying process.

- 12.78** Steam at  $100^{\circ}\text{C}$  causes more serious burns than water at  $100^{\circ}\text{C}$ . Why?

- 12.79 Vapor pressure measurements at several different temperatures are shown here for mercury. Determine graphically the molar heat of vaporization for mercury.

|   |      |      |       |       |       |
|---|------|------|-------|-------|-------|
| $t \text{ } (\text{ }^{\circ}\text{C})$ | 200  | 250  | 300   | 320   | 340   |
| $P \text{ (mmHg)}$                      | 17.3 | 74.4 | 246.8 | 376.3 | 557.9 |

- 12.80** The vapor pressure of benzene,  $\text{C}_6\text{H}_6$ , is 40.1 mmHg at  $7.6^{\circ}\text{C}$ . What is its vapor pressure at  $60.6^{\circ}\text{C}$ ? The molar heat of vaporization of benzene is 31.0 kJ/mol.

- 12.81 The vapor pressure of liquid X is lower than that of liquid Y at  $20^{\circ}\text{C}$ , but higher at  $60^{\circ}\text{C}$ . What can you deduce about the relative magnitude of the molar heats of vaporization of X and Y?

### Phase Diagrams

#### Review Questions

- 12.82 What is a phase diagram? What useful information can be obtained from a phase diagram?

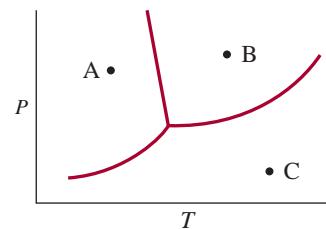
- 12.83 Explain how water's phase diagram differs from those of most substances. What property of water causes the difference?

### Problems

- 12.84** The blades of ice skates are quite thin, so the pressure exerted on ice by a skater can be substantial. Explain how this fact helps a person to skate on ice.

- 12.85 A length of wire is placed on top of a block of ice. The ends of the wire extend over the edges of the ice, and a heavy weight is attached to each end. It is found that the ice under the wire gradually melts, so that the wire slowly moves through the ice block. At the same time, the water above the wire refreezes. Explain the phase changes that accompany this phenomenon.

- 12.86** Consider the phase diagram of water shown here. Label the regions. Predict what would happen if we did the following: (a) Starting at A, we raise the temperature at constant pressure. (b) Starting at C, we lower the temperature at constant pressure. (c) Starting at B, we lower the pressure at constant temperature.



- 12.87 The boiling point and freezing point of sulfur dioxide are  $-10^{\circ}\text{C}$  and  $-72.7^{\circ}\text{C}$  (at 1 atm), respectively. The triple point is  $-75.5^{\circ}\text{C}$  and  $1.65 \times 10^{-3} \text{ atm}$ , and its critical point is at  $157^{\circ}\text{C}$  and 78 atm. On the basis of this information, draw a rough sketch of the phase diagram of  $\text{SO}_2$ .

### Additional Problems

- 12.88** Name the kinds of attractive forces that must be overcome to (a) boil liquid ammonia, (b) melt solid phosphorus ( $\text{P}_4$ ), (c) dissolve CsI in liquid HF, (d) melt potassium metal.

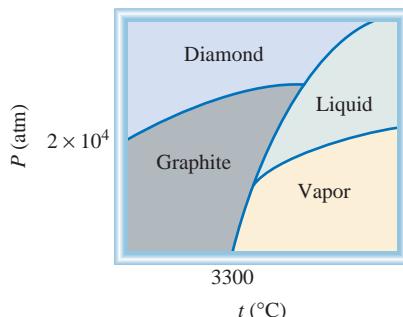
- 12.89 Which of these indicates very strong intermolecular forces in a liquid: (a) a very low surface tension, (b) a very low critical temperature, (c) a very low boiling point, (d) a very low vapor pressure?

- 12.90** At  $-35^{\circ}\text{C}$ , liquid HI has a higher vapor pressure than liquid HF. Explain.

- 12.91 From these properties of elemental boron, classify it as one of the crystalline solids discussed in Section 12.5: high melting point ( $2300^{\circ}\text{C}$ ), poor conductor

of heat and electricity, insoluble in water, very hard substance.

- 12.92** Referring to Figure 12.31, determine the stable phase of  $\text{CO}_2$  at (a) 4 atm and  $-60^\circ\text{C}$  and (b) 0.5 atm and  $-20^\circ\text{C}$ .
- 12.93** A solid contains X, Y, and Z atoms in a cubic lattice with X atoms in the corners, Y atoms in the body-centered positions, and Z atoms on the faces of the cell. What is the empirical formula of the compound?
- 12.94** A  $\text{CO}_2$  fire extinguisher is located on the outside of a building in Massachusetts. During the winter months, one can hear a sloshing sound when the extinguisher is gently shaken. In the summertime the sound is often absent. Explain. Assume that the extinguisher has no leaks and that it has not been used.
- 12.95** What is the vapor pressure of mercury at its normal boiling point ( $357^\circ\text{C}$ )?
- 12.96** A flask containing water is connected to a powerful vacuum pump. When the pump is turned on, the water begins to boil. After a few minutes, the same water begins to freeze. Eventually, the ice disappears. Explain what happens at each step.
- 12.97** The liquid-vapor boundary line in the phase diagram of any substance always stops abruptly at a certain point. Why?
- 12.98** Given the phase diagram of carbon shown here, answer these questions: (a) How many triple points are there and what are the phases that can coexist at each triple point? (b) Which has a higher density, graphite or diamond? (c) Synthetic diamond can be made from graphite. Using the phase diagram, how would you go about making diamond?



- 12.99** Estimate the molar heat of vaporization of a liquid whose vapor pressure doubles when the temperature is raised from  $85^\circ\text{C}$  to  $95^\circ\text{C}$ .

- 12.100** A student is given four samples of solids W, X, Y, and Z, all of which have a metallic luster. She is told that the solids are gold, lead sulfide, mica (which is quartz, or  $\text{SiO}_2$ ), and iodine. The results of her investigation are (a) W is a good electrical conductor; X, Y, and Z are poor electrical conductors; (b) when

the solids are hit with a hammer, W flattens out, X shatters into many pieces, Y is smashed into a powder, and Z is not affected; (c) when the solids are heated with a Bunsen burner, Y melts with some sublimation, but X, W, and Z do not melt; (d) in treatment with 6 M  $\text{HNO}_3$ , X dissolves; there is no effect on W, Y, or Z. On the basis of her studies, identify the solids.

- 12.101** Which of these statements are false: (a) Dipole-dipole interactions between molecules are greatest if the molecules possess only temporary dipole moments. (b) All compounds containing hydrogen atoms can participate in hydrogen bond formation. (c) Dispersion forces exist between all atoms, molecules, and ions. (d) The extent of ion-induced dipole interaction depends only on the charge on the ion.
- 12.102** The south pole of Mars is covered with dry ice, which partly sublimes during the summer. The  $\text{CO}_2$  vapor recondenses in the winter when the temperature drops to 150 K. Given that the heat of sublimation of  $\text{CO}_2$  is 25.9 kJ/mol, calculate the atmospheric pressure on the surface of Mars. [Hint: Use Figure 12.31 to determine the normal sublimation temperature of dry ice and Equation (12.4), which also applies to sublimation.]
- 12.103** The standard enthalpy of formation of gaseous molecular bromine is 30.7 kJ/mol. Use this information to calculate the molar heat of vaporization of molecular bromine at  $25^\circ\text{C}$ .
- 12.104** Heats of hydration, that is, heat changes that occur when ions become hydrated in solution, are largely due to ion-dipole interactions. The heats of hydration for the alkali metal ions are  $\text{Li}^+$ ,  $-520$  kJ/mol;  $\text{Na}^+$ ,  $-405$  kJ/mol;  $\text{K}^+$ ,  $-321$  kJ/mol. Account for the trend in these values.
- 12.105** A beaker of water is placed in a closed container. Predict the effect on the vapor pressure of the water when (a) its temperature is lowered, (b) the volume of the container is doubled, (c) more water is added to the beaker.
- 12.106** Ozone ( $\text{O}_3$ ) is a strong agent that can oxidize all the common metals except gold and platinum. A convenient test for ozone is based on its action on mercury. When exposed to ozone, mercury becomes dull looking and sticks to glass tubing (instead of flowing freely through it). Write a balanced equation for the reaction. What property of mercury is altered by its interaction with ozone?
- 12.107** A pressure cooker is a sealed container that allows steam to escape when it exceeds a predetermined pressure. How does this device reduce the time needed for cooking?
- 12.108** A 1.20-g sample of water is injected into an evacuated 5.00-L flask at  $65^\circ\text{C}$ . What percentage of the

water will be vapor when the system reaches equilibrium? Assume ideal behavior of water vapor and that the volume of liquid water is negligible. The vapor pressure of water at 65°C is 187.5 mmHg.

- 12.109 Swimming coaches sometimes suggest that a drop of alcohol (ethanol) placed in an ear plugged with water “draws out the water.” Explain this action from a molecular point of view.

- 12.110** Argon crystallizes in the face-centered cubic arrangement at 40 K. Given that the atomic radius of argon is 191 pm, calculate the density of solid argon.

- 12.111 Use the concept of intermolecular forces to explain why the far end of a walking cane rises when one raises the handle.

- 12.112** Why do citrus growers spray their trees with water to protect them from freezing?



- 12.113 What is the origin of dark spots on the inner glass walls of an old tungsten lightbulb? What is the purpose of filling these lightbulbs with argon gas?

- 12.114** A student heated a beaker of cold water (on a tripod) with a Bunsen burner. When the gas is ignited, she noticed that there was water condensed on the outside of the beaker. Explain what happened.

## SPECIAL PROBLEMS

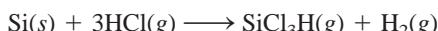
- 12.115 A quantitative measure of how efficiently spheres pack into unit cells is called *packing efficiency*, which is the percentage of the cell space occupied by the spheres. Calculate the packing efficiencies of a simple cubic cell, a body-centered cubic cell, and a face-centered cubic cell. (*Hint:* Refer to Figure 12.19 and use the relationship that the volume of a sphere is  $\frac{4}{3}\pi r^3$ , in which  $r$  is the radius of the sphere.)

- 12.116** A chemistry instructor performed the following mystery demonstration. Just before the students arrived in class, she heated some water to boiling in an Erlenmeyer flask. She then removed the flask from the flame and closed the flask with a rubber stopper. After the class commenced, she held the flask in front of the students and announced that she could make the water boil simply by rubbing an ice cube on the outside walls of the flask. To the amazement of everyone, it worked. Can you give the explanation for this phenomenon?

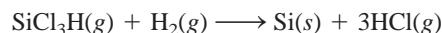
- 12.117 Silicon used in computer chips must have an impurity level below  $10^{-9}$  (that is, fewer than one impurity atom for every  $10^9$  Si atoms). Silicon is prepared by the reduction of quartz ( $\text{SiO}_2$ ) with coke (a form of carbon made by the destructive distillation of coal) at about 2000°C:



Next, solid silicon is separated from other solid impurities by treatment with hydrogen chloride at 350°C to form gaseous trichlorosilane ( $\text{SiCl}_3\text{H}$ ):



Finally, ultrapure Si can be obtained by reversing the above reaction at 1000°C:



(a) Trichlorosilane has a vapor pressure of 0.258 atm at  $-2^\circ\text{C}$ . What is its normal boiling point? Is trichlorosilane’s boiling point consistent with the type of intermolecular forces that exist among its molecules? (The molar heat of vaporization of trichlorosilane is 28.8 kJ/mol.) (b) What types of crystals do Si and  $\text{SiO}_2$  form? (c) Silicon has a diamond crystal structure (see Figure 12.22). Each cubic unit cell (edge length  $a = 543$  pm) contains eight Si atoms. If there are  $1.0 \times 10^{13}$  boron atoms per cubic centimeter in a sample of pure silicon, how many Si atoms are there for every B atom in the sample? Does this sample satisfy the  $10^{-9}$  purity requirement for the electronic grade silicon?

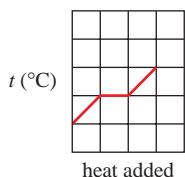
- 12.118** Iron crystallizes in a body-centered cubic lattice. The cell length as determined by X-ray diffraction is 286.7 pm. Given that the density of iron is 7.874 g/cm<sup>3</sup>, calculate Avogadro’s number.

- 12.119 The boiling point of methanol is 65.0°C and the standard enthalpy of formation of methanol vapor is  $-210.2$  kJ/mol. Calculate the vapor pressure of methanol (in mmHg) at 25°C. (*Hint:* See Appendix 2 for other thermodynamic data of methanol.)

- 12.120** An alkali metal in the form of a cube of edge length 0.171 cm is vaporized in a 0.843-L container at 1235 K. The vapor pressure is 19.2 mmHg. Identify the metal by calculating the atomic radius in picometers

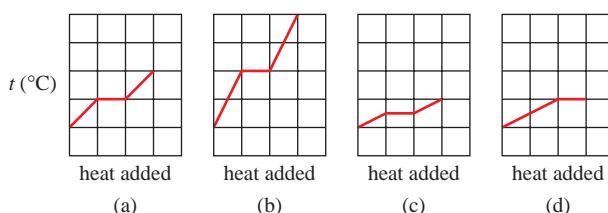
and the density. (*Hint:* You need to consult Figures 8.4, 12.19, and a chemistry handbook. All alkali metals form body-centered cubic lattices.)

- 12.121 A sample of water shows the following behavior as it is heated at a constant rate:



If twice the mass of water has the same amount of heat transferred to it, which of the following graphs

best describes the temperature variation? Note that the scales for all the graphs are the same.



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## ANSWERS TO PRACTICE EXERCISES

- 12.1** (a) Ionic and dispersion forces, (b) dispersion forces, (c) dipole-dipole and dispersion forces. **12.2**  $\text{CH}_3\text{OH}$ .

- 12.3**  $10.50 \text{ g/cm}^3$ . **12.4** Two. **12.5**  $369 \text{ mmHg}$ .

A sugar cube dissolving in water.  
The properties of a solution are markedly different from those of its solvent.



## Physical Properties of Solutions

### CHAPTER OUTLINE

- 13.1 Types of Solutions 426
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  - Using Colligative Properties to Determine Molar Mass •
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### ESSENTIAL CONCEPTS

**Solutions** There are many types of solutions; the most common is the liquid solution in which the solvent is a liquid and the solute is a solid or a liquid. Molecules that possess similar types of intermolecular forces readily mix with each other. Solubility is a quantitative measure of the amount of a solute dissolved in a solvent at a specific temperature.

**Concentration Units** The four common concentration units for solutions are percent by mass, mole fraction, molarity, and molality. Each one has its advantages and limitations.

**Effect of Temperature and Pressure on Solubility** Temperature generally has a marked influence on the solubility of a substance. Pressure can affect the solubility of a gas in a liquid but has little effect if the solute is a solid or liquid.

**Colligative Properties** The presence of a solute affects the vapor pressure, boiling point, and freezing point of a solvent. In addition, when a solution is separated from the solvent by a semipermeable membrane, osmosis, the passage of solvent molecules from the solvent to the solution, occurs. Equations have been derived that relate the extent of the changes in these properties to the concentration of the solution.

### Interactive Activity Summary

- 1. Animation: Dissolution of an Ionic and a Covalent Compound (13.2)
- 2. Animation: Osmosis (13.6)
- 3. Interactivity: Test Solution with Electrolytes (13.6)

## 13.1 Types of Solutions

Most chemical reactions take place not between pure solids, liquids, or gases, but among ions and molecules dissolved in water or other solvents. In Section 4.1 we noted that a solution is a homogeneous mixture of two or more substances. Because this definition places no restriction on the nature of the substances involved, we can distinguish six types of solutions, depending on the original states (solid, liquid, or gas) of the solution components. Table 13.1 gives examples of each of these types.

Our focus here will be on solutions involving at least one liquid component—that is, gas-liquid, liquid-liquid, and solid-liquid solutions. And, perhaps not too surprisingly, the liquid solvent in most of the solutions we will study is water.

Chemists also characterize solutions by their capacity to dissolve a solute. A *solution that contains the maximum amount of a solute in a given solvent, at a specific temperature*, is called a **saturated solution**. Before the saturation point is reached, the solution is said to be **unsaturated**; it *contains less solute than it has the capacity to dissolve*. A third type, a **supersaturated solution**, *contains more solute than is present in a saturated solution*. Supersaturated solutions are not very stable. In time, some of the solute will come out of a supersaturated solution as crystals. *The process in which dissolved solute comes out of solution and forms crystals* is called **crystallization**. Note that both precipitation and crystallization describe the separation of excess solid substance from a supersaturated solution. However, solids formed by the two processes differ in appearance. We normally think of precipitates as being made up of small particles, whereas crystals may be large and well formed (Figure 13.1).

## 13.2 A Molecular View of the Solution Process

In liquids and solids, molecules are held together by intermolecular attractions. These forces also play a central role in the formation of solutions. When one substance (the solute) dissolves in another (the solvent), particles of the solute disperse throughout the solvent. The solute particles occupy positions that are normally taken by solvent molecules. The ease with which a solute particle replaces a solvent molecule depends on the relative strengths of three types of interactions:

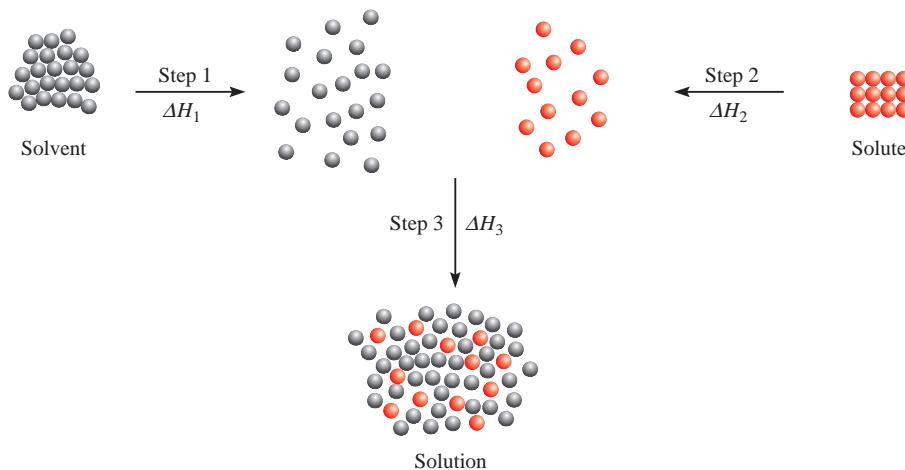
- solvent-solvent interaction
- solute-solute interaction
- solvent-solute interaction



**Figure 13.1**  
In a supersaturated sodium acetate solution (top), sodium acetate crystals rapidly form when a small seed crystal is added.

**TABLE 13.1** Types of Solutions

| Solute | Solvent | State of Resulting Solution | Examples                             |
|--------|---------|-----------------------------|--------------------------------------|
| Gas    | Gas     | Gas                         | Air                                  |
| Gas    | Liquid  | Liquid                      | Soda water ( $\text{CO}_2$ in water) |
| Gas    | Solid   | Solid                       | $\text{H}_2$ gas in palladium        |
| Liquid | Liquid  | Liquid                      | Ethanol in water                     |
| Solid  | Liquid  | Liquid                      | $\text{NaCl}$ in water               |
| Solid  | Solid   | Solid                       | Brass (Cu/Zn), solder (Sn/Pb)        |

**Figure 13.2**

*A molecular view of the solution process portrayed as taking place in three steps: First the solvent and solute molecules are separated (steps 1 and 2). Then the solvent and solute molecules mix (step 3).*

For simplicity, we can imagine the solution process taking place in three distinct steps (Figure 13.2). Step 1 is the separation of solvent molecules, and step 2 entails the separation of solute molecules. These steps require energy input to break attractive intermolecular forces; therefore, they are endothermic. In step 3 the solvent and solute molecules mix. This step may be exothermic or endothermic. The heat of solution  $\Delta H_{\text{soln}}$  is given by

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3 \quad (13.1)$$

If the solute-solvent attraction is stronger than the solvent-solvent attraction and solute-solute attraction, the solution process is favorable: that is, it is exothermic ( $\Delta H_{\text{soln}} < 0$ ). If the solute-solvent interaction is weaker than the solvent-solvent and solute-solute interactions, the solution process is endothermic ( $\Delta H_{\text{soln}} > 0$ ).

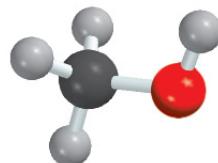
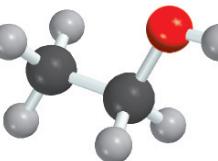
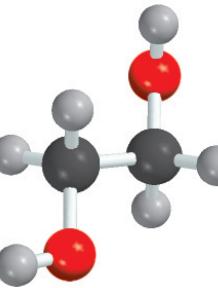
You may wonder why a solute dissolves in a solvent at all if the attraction among its own molecules is stronger than that between its molecules and the solvent molecules. The solution process, like all physical and chemical processes, is governed by two factors. One is energy, which determines whether a solution process is exothermic or endothermic. The second factor is an inherent tendency toward disorder in all natural events. In much the same way that a deck of new playing cards becomes mixed up after it has been shuffled a few times, when solute and solvent molecules mix to form a solution, there is an increase in randomness or disorder. In the pure state, the solvent and solute possess a fair degree of order, characterized by the more or less regular arrangement of atoms, molecules, or ions in three-dimensional space. Much of this order is destroyed when the solute dissolves in the solvent (see Figure 13.2). Therefore, the solution process is accompanied by an increase in disorder or randomness. It is the increase in disorder of the system that favors the solubility of any substance, even if the solution process is endothermic.

Solubility is a measure of the amount of a solute that will dissolve in a solvent at a specific temperature. The saying “like dissolves like” helps in predicting the solubility of a substance in a solvent. What this expression means is that two substances with intermolecular forces of similar type and magnitude are likely to be soluble in each other. For example, both carbon tetrachloride ( $\text{CCl}_4$ ) and benzene ( $\text{C}_6\text{H}_6$ ) are nonpolar liquids. The only intermolecular forces present in these substances are dispersion forces (see Section 12.2). When these two liquids are mixed, they readily

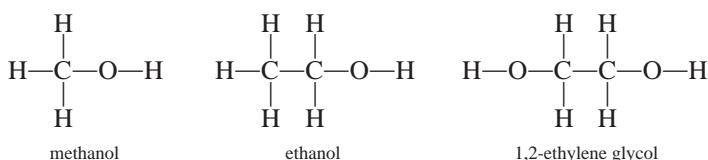


**Animation:**  
Dissolution of an Ionic and a  
Covalent Compound  
[ARIS Animations](#)

This equation is an application of Hess's law.

CH<sub>3</sub>OHC<sub>2</sub>H<sub>5</sub>OHCH<sub>2</sub>(OH)CH<sub>2</sub>(OH)

dissolve in each other, because the attraction between CCl<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> molecules is comparable in magnitude to that between CCl<sub>4</sub> molecules and between C<sub>6</sub>H<sub>6</sub> molecules. When *two liquids are completely soluble in each other in all proportions*, as in this case, they are said to be **miscible**. Alcohols such as methanol, ethanol, and ethylene glycol are miscible with water because of their ability to form hydrogen bonds with water molecules:



When sodium chloride dissolves in water, the ions are stabilized in solution by hydration, which involves ion-dipole interaction. In general, we predict that ionic compounds should be much more soluble in polar solvents, such as water, liquid ammonia, and liquid hydrogen fluoride, than in nonpolar solvents, such as benzene and carbon tetrachloride. Because the molecules of nonpolar solvents lack a dipole moment, they cannot effectively solvate the Na<sup>+</sup> and Cl<sup>-</sup> ions. (**Solvation** is the process in which an ion or a molecule is surrounded by solvent molecules arranged in a specific manner. When the solvent is water, the process is called *hydration*.) The predominant intermolecular interaction between ions and nonpolar compounds is ion-induced dipole interaction, which is much weaker than ion-dipole interaction. Consequently, ionic compounds usually have extremely low solubility in nonpolar solvents.

### Example 13.1

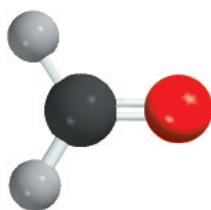
Predict the relative solubilities in the following cases: (a) Bromine (Br<sub>2</sub>) in benzene (C<sub>6</sub>H<sub>6</sub>,  $\mu = 0$  D) and in water ( $\mu = 1.87$  D), (b) KCl in carbon tetrachloride (CCl<sub>4</sub>,  $\mu = 0$  D) and in liquid ammonia (NH<sub>3</sub>,  $\mu = 1.46$  D), (c) formaldehyde (CH<sub>2</sub>O) in carbon disulfide (CS<sub>2</sub>,  $\mu = 0$ ) and in water.

**Strategy** In predicting solubility, remember the saying: Like dissolves like. A nonpolar solute will dissolve in a nonpolar solvent; ionic compounds will generally dissolve in polar solvents due to favorable ion-dipole interaction; solutes that can form hydrogen bonds with the solvent will have high solubility in the solvent.

**Solution** (a) Br<sub>2</sub> is a nonpolar molecule and therefore should be more soluble in C<sub>6</sub>H<sub>6</sub>, which is also nonpolar, than in water. The only intermolecular forces between Br<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> are dispersion forces.

(b) KCl is an ionic compound. For it to dissolve, the individual K<sup>+</sup> and Cl<sup>-</sup> ions must be stabilized by ion-dipole interaction. Because CCl<sub>4</sub> has no dipole moment, KCl should be more soluble in liquid NH<sub>3</sub>, a polar molecule with a large dipole moment.

(c) Because CH<sub>2</sub>O is a polar molecule and CS<sub>2</sub> (a linear molecule) is nonpolar,

CH<sub>2</sub>O

(Continued)

the forces between molecules of  $\text{CH}_2\text{O}$  and  $\text{CS}_2$  are dipole-induced dipole and dispersion. On the other hand,  $\text{CH}_2\text{O}$  can form hydrogen bonds with water, so it should be more soluble in that solvent.

**Similar problem:** 13.9.

**Practice Exercise** Is iodine ( $\text{I}_2$ ) more soluble in water or in carbon disulfide ( $\text{CS}_2$ )?

## 13.3 Concentration Units

Quantitative study of a solution requires that we know its *concentration*, that is, the amount of solute present in a given amount of solution. Chemists use several different concentration units, each of which has advantages as well as limitations. Let us examine the three most common units of concentration: percent by mass, molarity, and molality.

### Types of Concentration Units

#### Percent by Mass

The *percent by mass* (also called the *percent by weight* or the *weight percent*) is defined as

$$\text{percent by mass of solute} = \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100\%$$

$$= \frac{\text{mass of solute}}{\text{mass of soln}} \times 100\% \quad (13.2)$$

The percent by mass has no units because it is a ratio of two similar quantities.

#### Molarity ( $M$ )

The molarity unit was defined in Section 4.5 as the number of moles of solute in 1 L of solution; that is,

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of soln}} \quad (13.3)$$

**For calculations involving molarity, see Example 4.5 on p. 116.**

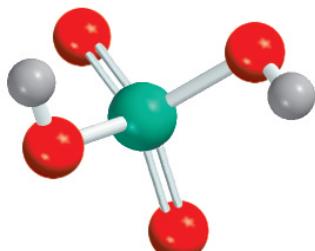
Thus, molarity has the units of mole per liter (mol/L).

#### Molality ( $m$ )

*Molality* is the number of moles of solute dissolved in 1 kg (1000 g) of solvent—that is,

$$\text{molality} = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} \quad (13.4)$$

For example, to prepare a 1 *molal*, or 1 *m*, sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) aqueous solution, we need to dissolve 1 mole (142.0 g) of the substance in 1000 g (1 kg) of water. Depending on the nature of the solute-solvent interaction, the final volume of the solution will be either greater or less than 1000 mL. It is also possible, though very unlikely, that the final volume could be equal to 1000 mL.



### Example 13.2

Calculate the molality of a sulfuric acid solution containing 24.4 g of sulfuric acid in 198 g of water. The molar mass of sulfuric acid is 98.08 g.

**Strategy** To calculate the molality of a solution, we need to know the number of moles of solute and the mass of the solvent in kilograms.

**Solution** The definition of molality ( $m$ ) is

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

First, we find the number of moles of sulfuric acid in 24.4 g of the acid, using its molar mass as the conversion factor:

$$\begin{aligned} \text{moles of H}_2\text{SO}_4 &= 24.4 \cancel{\text{g H}_2\text{SO}_4} \times \frac{1 \text{ mol H}_2\text{SO}_4}{98.09 \cancel{\text{g H}_2\text{SO}_4}} \\ &= 0.249 \text{ mol H}_2\text{SO}_4 \end{aligned}$$

The mass of water is 198 g, or 0.198 kg. Therefore,

$$\begin{aligned} \text{molality} &= \frac{0.249 \text{ mol H}_2\text{SO}_4}{0.198 \text{ kg H}_2\text{O}} \\ &= 1.26 \text{ } m \end{aligned}$$

**Similar problem:** 13.15.

**Practice Exercise** What is the molality of a solution containing 7.78 g of urea [ $(\text{NH}_2)_2\text{CO}$ ] in 203 g of water?

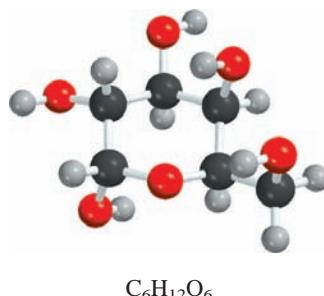
### Comparison of Concentration Units

The choice of a concentration unit is based on the purpose of the experiment. The advantage of molarity is that it is generally easier to measure the volume of a solution, using precisely calibrated volumetric flasks, than to weigh the solvent, as we saw in Section 4.5. For this reason, molarity is often preferred over molality. On the other hand, molality is independent of temperature, because the concentration is expressed in number of moles of solute and mass of solvent. The volume of a solution typically increases with increasing temperature, so that a solution that is 1.0  $M$  at 25°C may become 0.97  $M$  at 45°C because of the increase in volume. This concentration dependence on temperature can significantly affect the accuracy of an experiment. Therefore, it is sometimes preferable to use molality instead of molarity.

Percent by mass is similar to molality in that it is independent of temperature. Furthermore, because it is defined in terms of ratio of mass of solute to mass of solution, we do not need to know the molar mass of the solute to calculate the percent by mass.

Sometimes it is desirable to convert one concentration unit of a solution to another; for example, the same solution may be employed for different experiments that require different concentration units for calculations. Suppose we want to express the concentration of a 0.396  $m$  glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) solution in molarity. We know there is 0.396 mole of glucose in 1000 g of the solvent and we need to determine the volume of this solution to calculate molarity. First, we calculate the mass of the solution from the molar mass of glucose:

$$\left( 0.396 \cancel{\text{mol C}_6\text{H}_{12}\text{O}_6} \times \frac{180.2 \text{ g}}{1 \cancel{\text{mol C}_6\text{H}_{12}\text{O}_6}} \right) + 1000 \text{ g H}_2\text{O soln} = 1071 \text{ g}$$



The next step is to experimentally determine the density of the solution, which is found to be 1.16 g/mL. We can now calculate the volume of the solution in liters by writing

$$\begin{aligned}\text{volume} &= \frac{\text{mass}}{\text{density}} \\ &= \frac{1071 \text{ g}}{1.16 \text{ g/mL}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \\ &= 0.923 \text{ L}\end{aligned}$$

Finally, the molarity of the solution is given by

$$\begin{aligned}\text{molarity} &= \frac{\text{moles of solute}}{\text{liters of soln}} \\ &= \frac{0.396 \text{ mol}}{0.923 \text{ L}} \\ &= 0.429 \text{ mol/L} = 0.429 M\end{aligned}$$

As you can see, the density of the solution serves as a conversion factor between molality and molarity.

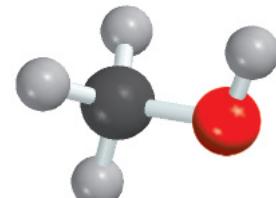
### Example 13.3

The density of a 2.45 M aqueous solution of methanol ( $\text{CH}_3\text{OH}$ ) is 0.976 g/mL. What is the molality of the solution? The molar mass of methanol is 32.04 g.

**Strategy** To calculate the molality, we need to know the number of moles of methanol and the mass of solvent in kilograms. We assume 1 L of solution, so the number of moles of methanol is 2.45 mol.

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

want to calculate      given  
need to find



$\text{CH}_3\text{OH}$

**Solution** Our first step is to calculate the mass of water in one liter of the solution, using density as a conversion factor. The total mass of 1 L of a 2.45 M solution of methanol is

$$1 \text{ L soln} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \times \frac{0.976 \text{ g}}{1 \text{ mL soln}} = 976 \text{ g}$$

Because this solution contains 2.45 moles of methanol, the amount of water (solvent) in the solution is

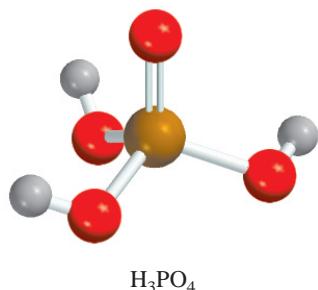
$$\begin{aligned}\text{mass of H}_2\text{O} &= \text{mass of soln} - \text{mass of solute} \\ &= 976 \text{ g} - \left( 2.45 \text{ mol CH}_3\text{OH} \times \frac{32.04 \text{ g CH}_3\text{OH}}{1 \text{ mol CH}_3\text{OH}} \right) \\ &= 898 \text{ g}\end{aligned}$$

The molality of the solution can be calculated by converting 898 g to 0.898 kg:

$$\begin{aligned}\text{molality} &= \frac{2.45 \text{ mol CH}_3\text{OH}}{0.898 \text{ kg H}_2\text{O}} \\ &= 2.73 m\end{aligned}$$

**Similar problem: 13.16(a).**

**Practice Exercise** Calculate the molality of a 5.86 M ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) solution whose density is 0.927 g/mL.



### Example 13.4

Calculate the molality of a 35.4 percent (by mass) aqueous solution of phosphoric acid ( $\text{H}_3\text{PO}_4$ ). The molar mass of phosphoric acid is 98.00 g.

**Strategy** In solving this type of problem, it is convenient to assume that we start with 100.0 g of the solution. If the mass of phosphoric acid is 35.4 percent, or 35.4 g, the percent by mass and mass of water must be  $100.0\% - 35.4\% = 64.6\%$  and 64.6 g.

**Solution** From the known molar mass of phosphoric acid, we can calculate the molality in two steps, as shown in Example 13.2. First we calculate the number of moles of phosphoric acid in 35.4 g of the acid:

$$\begin{aligned}\text{moles of H}_3\text{PO}_4 &= 35.4 \text{ g H}_3\text{PO}_4 \times \frac{1 \text{ mol H}_3\text{PO}_4}{97.99 \text{ g H}_3\text{PO}_4} \\ &= 0.361 \text{ mol H}_3\text{PO}_4\end{aligned}$$

The mass of water is 64.6 g, or 0.0646 kg. Therefore, the molality is given by

$$\begin{aligned}\text{molality} &= \frac{0.361 \text{ mol H}_3\text{PO}_4}{0.0646 \text{ kg H}_2\text{O}} \\ &= 5.59 \text{ m}\end{aligned}$$

**Similar problem:** 13.16(b).

**Practice Exercise** Calculate the molality of a 44.6 percent (by mass) aqueous solution of sodium chloride.

## 13.4 Effect of Temperature on Solubility

Recall that solubility is defined as the maximum amount of a solute that will dissolve in a given quantity of solvent *at a specific temperature*. For most substances, temperature affects solubility. In this section we will consider the effects of temperature on the solubility of solids and gases.

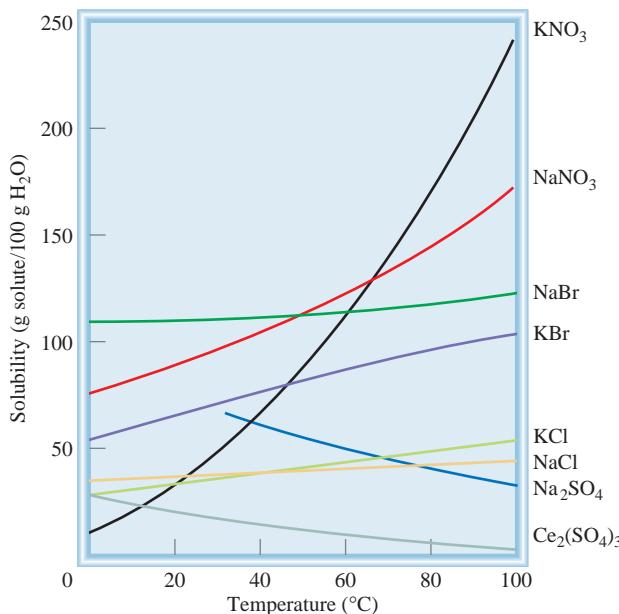
### Solid Solubility and Temperature

Figure 13.3 shows the temperature dependence of the solubility of some ionic compounds in water. In most but certainly not all cases, the solubility of a solid substance increases with temperature. However, there is no clear correlation between the sign of  $\Delta H_{\text{soln}}$  and the variation of solubility with temperature. For example, the solution process of  $\text{CaCl}_2$  is exothermic and that of  $\text{NH}_4\text{NO}_3$  is endothermic. But the solubility of both compounds increases with increasing temperature. In general, the effect of temperature on solubility is best determined experimentally.

### Gas Solubility and Temperature

The solubility of gases in water usually decreases with increasing temperature (Figure 13.4). When water is heated in a beaker, you can see bubbles of air forming on the side of the glass before the water boils. As the temperature rises, the dissolved air molecules begin to “boil out” of the solution long before the water itself boils.

The reduced solubility of molecular oxygen in hot water has a direct bearing on *thermal pollution*, that is, *the heating of the environment—usually waterways—to temperatures that are harmful to its living inhabitants*. It is estimated that every year



**Figure 13.3**  
Dependence on temperature of the solubility of some ionic compounds in water.

in the United States some 100,000 billion gallons of water are used for industrial cooling, mostly in electric power and nuclear power production. This process heats up the water, which is then returned to the rivers and lakes from which it was taken. Ecologists have become increasingly concerned about the effect of thermal pollution on aquatic life. Fish, like all other cold-blooded animals, have much more difficulty coping with rapid temperature fluctuation in the environment than humans do. An increase in water temperature accelerates their rate of metabolism, which generally doubles with each 10°C rise. The speedup of metabolism increases the fish's need for oxygen at the same time that the supply of oxygen decreases because of its lower solubility in heated water. Effective ways to cool power plants while doing only minimal damage to the biological environment are being sought.

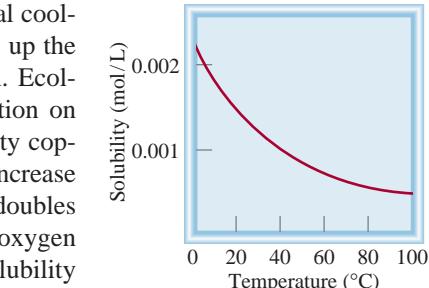
On the lighter side, a knowledge of the variation of gas solubility with temperature can improve one's performance in a popular recreational sport—fishing. On a hot summer day, an experienced fisherman usually picks a deep spot in the river or lake to cast the bait. Because the oxygen content is greater in the deeper, cooler region, most fish will be found there.

## 13.5 Effect of Pressure on the Solubility of Gases

For all practical purposes, external pressure has no influence on the solubilities of liquids and solids, but it does greatly affect the solubility of gases. The quantitative relationship between gas solubility and pressure is given by **Henry's law**, which states that *the solubility of a gas in a liquid is proportional to the pressure of the gas over the solution:*

$$c \propto P$$

$$c = kP$$

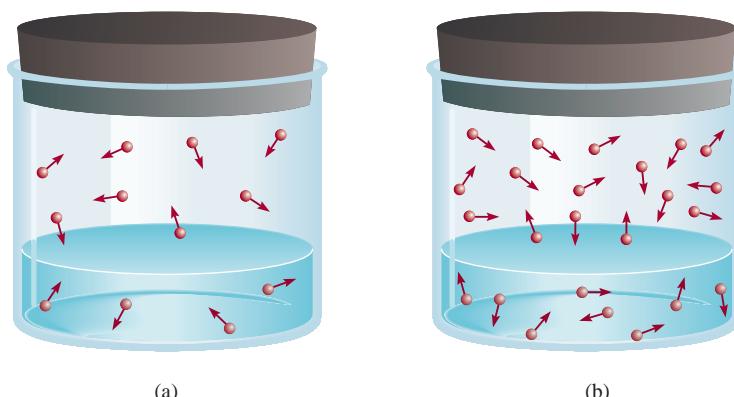


**Figure 13.4**  
Dependence on temperature of the solubility of O<sub>2</sub> gas in water. Note that the solubility decreases as temperature increases. The pressure of the gas over the solution is 1 atm.

Here  $c$  is the molar concentration (moles per liter) of the dissolved gas;  $P$  is the pressure (in atmospheres) of the gas over the solution; and, for a given gas,  $k$  is a constant

**Figure 13.5**

A molecular interpretation of Henry's law. When the partial pressure of the gas over the solution increases from (a) to (b), the concentration of the dissolved gas also increases according to Equation (13.5).



**Each gas has a different  $k$  value at a given temperature.**

that depends only on temperature. The constant  $k$  has the units mol/L · atm. You can see that when the pressure of the gas is 1 atm,  $c$  is *numerically* equal to  $k$ .

Henry's law can be understood qualitatively in terms of the kinetic molecular theory. The amount of gas that will dissolve in a solvent depends on how frequently the molecules in the gas phase collide with the liquid surface and become trapped by the condensed phase. Suppose we have a gas in dynamic equilibrium with a solution [Figure 13.5(a)]. At every instant, the number of gas molecules entering the solution is equal to the number of dissolved molecules moving into the gas phase. When the partial pressure is increased, more molecules dissolve in the liquid because more molecules are striking the surface of the liquid. This process continues until the concentration of the solution is again such that the number of molecules leaving the solution per second equals the number entering the solution [Figure 13.5(b)]. Because of the increased concentration of molecules in both the gas and solution phases, this number is greater in (b) than in (a), where the partial pressure is lower.

A practical demonstration of Henry's law is the effervescence of a soft drink when the cap of the bottle is removed. Before the beverage bottle is sealed, it is pressurized with a mixture of air and CO<sub>2</sub> saturated with water vapor. Because of the high partial pressure of CO<sub>2</sub> in the pressurizing gas mixture, the amount dissolved in the soft drink is many times the amount that would dissolve under normal atmospheric conditions. When the cap is removed, the pressurized gases escape, eventually the pressure in the bottle falls to atmospheric pressure, and the amount of CO<sub>2</sub> remaining in the beverage is determined only by the normal atmospheric partial pressure of CO<sub>2</sub>, 0.0003 atm. The excess dissolved CO<sub>2</sub> comes out of solution, causing the effervescence.



The effervescence of a soft drink. The bottle was shaken before being opened to dramatize the escape of CO<sub>2</sub>.

### Example 13.5

The solubility of nitrogen gas at 25°C and 1 atm is  $6.8 \times 10^{-4}$  mol/L. What is the concentration of nitrogen dissolved in water under atmospheric conditions? The partial pressure of nitrogen gas in the atmosphere is 0.78 atm.

**Strategy** The given solubility enables us to calculate Henry's law constant ( $k$ ), which can then be used to determine the concentration of the solution.

**Solution** The first step is to calculate the quantity  $k$  in Equation (13.5):

$$\begin{aligned} c &= kP \\ 6.8 \times 10^{-4} \text{ mol/L} &= k(1 \text{ atm}) \\ k &= 6.8 \times 10^{-4} \text{ mol/L} \cdot \text{atm} \end{aligned}$$

(Continued)

Therefore, the solubility of nitrogen gas in water is

$$\begin{aligned} c &= (6.8 \times 10^{-4} \text{ mol/L} \cdot \text{atm})(0.78 \text{ atm}) \\ &= 5.3 \times 10^{-4} \text{ mol/L} \\ &= 5.3 \times 10^{-4} M \end{aligned}$$

The decrease in solubility is the result of lowering the pressure from 1 atm to 0.78 atm.

**Check** The ratio of the concentrations [ $(5.3 \times 10^{-4} M / 6.8 \times 10^{-4} M) = 0.78$ ] should be equal to the ratio of the pressures ( $0.78 \text{ atm} / 1.0 \text{ atm} = 0.78$ ).

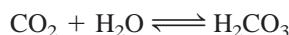
**Similar problem:** 13.35.

**Practice Exercise** Calculate the molar concentration of oxygen in water at 25°C for a partial pressure of 0.22 atm. The Henry's law constant for oxygen is  $1.3 \times 10^{-3} \text{ mol/L} \cdot \text{atm}$ .

Most gases obey Henry's law, but there are some important exceptions. For example, if the dissolved gas *reacts* with water, higher solubilities can result. The solubility of ammonia is much higher than expected because of the reaction



Carbon dioxide also reacts with water, as follows:



Another interesting example is the dissolution of molecular oxygen in blood. Normally, oxygen gas is only sparingly soluble in water (see the Practice Exercise in Example 13.5). However, its solubility in blood is dramatically greater because of the high content of hemoglobin (Hb) molecules. Each hemoglobin molecule can bind up to four oxygen molecules, which are eventually delivered to the tissues for use in metabolism:



This is the process that accounts for the high solubility of molecular oxygen in blood.

## 13.6 Colligative Properties

Several important properties of solutions depend on the number of solute particles in solution and not on the nature of the solute particles. These properties are called **colligative properties** (or collective properties) because they are bound together by a common origin; that is, they all depend on the number of solute particles present, whether these particles are atoms, ions, or molecules. The colligative properties are vapor-pressure lowering, boiling-point elevation, freezing-point depression, and osmotic pressure. We will first discuss the colligative properties of nonelectrolyte solutions. It is important to keep in mind that we are talking about relatively dilute solutions, that is, solutions whose concentrations are  $\leq 0.2 M$ .

### Vapor-Pressure Lowering

If a solute is **nonvolatile** (that is, it *does not have a measurable vapor pressure*), the vapor pressure of its solution is always less than that of the pure solvent. Thus, the relationship between solution vapor pressure and solvent vapor pressure depends on the concentration of the solute in the solution. This relationship is given by **Raoult's**

To review the concept of equilibrium vapor pressure as it applies to pure liquids, see Section 12.6.

**law** (after the French chemist Francois Raoult), which states that *the partial pressure of a solvent over a solution,  $P_1$ , is given by the vapor pressure of the pure solvent,  $P_1^\circ$ , times the mole fraction of the solvent in the solution,  $X_1$* :

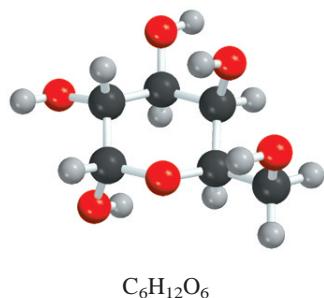
$$P_1 = X_1 P_1^\circ \quad (13.6)$$

In a solution containing only one solute,  $X_1 = 1 - X_2$ , in which  $X_2$  is the mole fraction of the solute (see Section 5.5). Equation (13.6) can therefore be rewritten as

$$P_1 = (1 - X_2) P_1^\circ$$

$$P_1^\circ - P_1 = \Delta P = X_2 P_1^\circ \quad (13.7)$$

We see that the *decrease* in vapor pressure,  $\Delta P$ , is directly proportional to the concentration (measured in mole fraction) of the solute present.



### Example 13.6

Calculate the vapor pressure of a solution made by dissolving 218 g of glucose (molar mass = 180.2 g/mol) in 460 mL of water at 30°C. What is the vapor-pressure lowering? The vapor pressure of pure water at 30°C is given in Table 5.2. Assume the density of the solution is 1.00 g/mL.

**Strategy** We need Raoult's law [Equation (13.6)] to determine the vapor pressure of a solution. Note that glucose is a nonvolatile solute.

**Solution** The vapor pressure of a solution ( $P_1$ ) is

$$P_1 = X_1 P_1^\circ$$

want to calculate need to find

given

First we calculate the number of moles of glucose and water in the solution:

$$n_1(\text{water}) = 460 \text{ mL} \times \frac{1.00 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 25.5 \text{ mol}$$

$$n_2(\text{glucose}) = 218 \text{ g} \times \frac{1 \text{ mol}}{180.2 \text{ g}} = 1.21 \text{ mol}$$

The mole fraction of water,  $X_1$ , is given by

$$\begin{aligned} X_1 &= \frac{n_1}{n_1 + n_2} \\ &= \frac{25.5 \text{ mol}}{25.5 \text{ mol} + 1.21 \text{ mol}} = 0.955 \end{aligned}$$

From Table 5.2, we find the vapor pressure of water at 30°C to be 31.82 mmHg. Therefore, the vapor pressure of the glucose solution is

$$\begin{aligned} P_1 &= 0.955 \times 31.82 \text{ mmHg} \\ &= 30.4 \text{ mmHg} \end{aligned}$$

Finally, the vapor-pressure lowering is  $(31.82 - 30.4) \text{ mmHg}$ , or 1.4 mmHg.

*(Continued)*

**Check** We can also calculate the vapor pressure lowering by using Equation (13.7). Because the mole fraction of glucose is  $(1 - 0.955)$ , or 0.045, the vapor pressure lowering is given by  $(0.045)(31.82 \text{ mmHg})$  or 1.4 mmHg.

Similar problems: 13.49, 13.50.

**Practice Exercise** Calculate the vapor pressure of a solution made by dissolving 82.4 g of urea (molar mass = 60.06 g/mol) in 212 mL of water at 35°C. What is the vapor-pressure lowering?

Why is the vapor pressure of a solution less than that of its pure solvent? As was mentioned in Section 13.2, one driving force in physical and chemical processes is the increase in disorder—the greater the disorder created, the more favorable the process. Vaporization increases the disorder of a system because molecules in a vapor have less order than those in a liquid. Because a solution is more disordered than a pure solvent, the difference in disorder between a solution and a vapor is less than that between a pure solvent and a vapor. Thus, solvent molecules have less of a tendency to leave a solution than to leave the pure solvent to become vapor, and the vapor pressure of a solution is less than that of the solvent.

If both components of a solution are **volatile** (that is, *have measurable vapor pressure*), the vapor pressure of the solution is the sum of the individual partial pressures. Raoult's law holds equally well in this case:

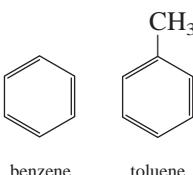
$$P_A = X_A P_A^\circ$$

$$P_B = X_B P_B^\circ$$

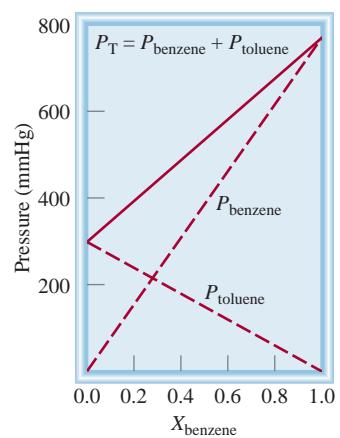
in which  $P_A$  and  $P_B$  are the partial pressures over the solution for components A and B;  $P_A^\circ$  and  $P_B^\circ$  are the vapor pressures of the pure substances; and  $X_A$  and  $X_B$  are their mole fractions. The total pressure is given by Dalton's law of partial pressure (see Section 5.5):

$$P_T = P_A + P_B$$

Benzene and toluene have similar structures and therefore similar intermolecular forces:



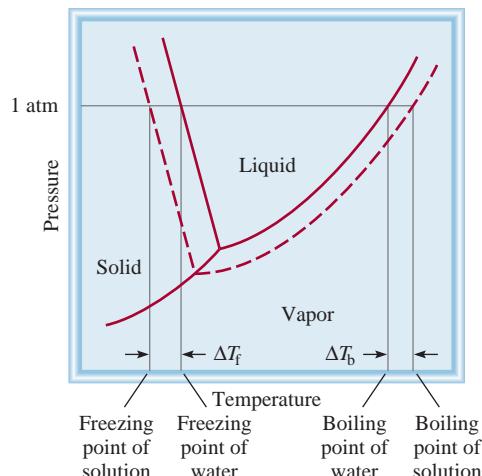
In a solution of benzene and toluene, the vapor pressure of each component obeys Raoult's law. Figure 13.6 shows the dependence of the total vapor pressure ( $P_T$ ) in a benzene-toluene solution on the composition of the solution. Note that we need only express the composition of the solution in terms of the mole fraction of one component. For every value of  $X_{\text{benzene}}$ , the mole fraction of toluene is given by  $(1 - X_{\text{benzene}})$ . The benzene-toluene solution is one of the few examples of an **ideal solution**, which is *any solution that obeys Raoult's law*. One characteristic of an ideal solution is that the intermolecular forces between solute and solvent molecules are equal to those between solute molecules and between solvent molecules. Consequently, the heat of solution,  $\Delta H_{\text{soln}}$ , is always zero.



**Figure 13.6**  
The dependence of the partial pressures of benzene and toluene on their mole fractions in a benzene-toluene solution ( $X_{\text{toluene}} = 1 - X_{\text{benzene}}$ ) at 80°C. This solution is said to be ideal because the vapor pressures obey Raoult's law.

**Figure 13.7**

Phase diagram illustrating the boiling-point elevation and freezing-point depression of aqueous solutions. The dashed curves pertain to the solution, and the solid curves to the pure solvent. As you can see, the boiling point of the solution is higher than that of water, and the freezing point of the solution is lower than that of water.



### Boiling-Point Elevation

Because the presence of a *nonvolatile* solute lowers the vapor pressure of a solution, it must also affect the boiling point of the solution. The boiling point of a solution is the temperature at which its vapor pressure equals the external atmospheric pressure (see Section 12.6). Figure 13.7 shows the phase diagram of water and the changes that occur in an aqueous solution. Because at any temperature the vapor pressure of the solution is lower than that of the pure solvent, the liquid-vapor curve for the solution lies below that for the pure solvent. Consequently, the solution curve (dotted line) intersects the horizontal line that marks  $P = 1 \text{ atm}$  at a *higher* temperature than the normal boiling point of the pure solvent. This graphical analysis shows that the boiling point of the solution is higher than that of water. The *boiling-point elevation*,  $\Delta T_b$ , is defined as

$$\Delta T_b = T_b - T_b^\circ$$

in which  $T_b$  is the boiling point of the solution and  $T_b^\circ$  the boiling point of the pure solvent. Because  $\Delta T_b$  is proportional to the vapor-pressure lowering, it is also proportional to the concentration (molality) of the solution. That is,

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m \quad (13.8)$$

in which  $m$  is the molality of the solution and  $K_b$  is the *molal boiling-point elevation constant*. The units of  $K_b$  are  $^{\circ}\text{C}/m$ .

It is important to understand the choice of concentration unit here. We are dealing with a system (the solution) whose temperature is *not* kept constant, so we cannot express the concentration units in molarity because molarity changes with temperature.

Table 13.2 lists the value of  $K_b$  for several common solvents. Using the boiling-point elevation constant for water and Equation (13.8), you can see that if the molality of an aqueous solution is 1.00  $m$ , the boiling point will be  $100.52^{\circ}\text{C}$ .

### Freezing-Point Depression

A nonscientist may remain forever unaware of the boiling-point elevation phenomenon, but a careful observer living in a cold climate is familiar with freezing-point depression. Ice on frozen roads and sidewalks melts when sprinkled with salts such



De-icing of airplanes is based on freezing-point depression.

**TABLE 13.2****Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids**

| Solvent     | Normal Freezing Point (°C)* | $K_f$ (°C/m) | Normal Boiling Point (°C)* | $K_b$ (°C/m) |
|-------------|-----------------------------|--------------|----------------------------|--------------|
| Water       | 0                           | 1.86         | 100                        | 0.52         |
| Benzene     | 5.5                         | 5.12         | 80.1                       | 2.53         |
| Ethanol     | -117.3                      | 1.99         | 78.4                       | 1.22         |
| Acetic acid | 16.6                        | 3.90         | 117.9                      | 2.93         |
| Cyclohexane | 6.6                         | 20.0         | 80.7                       | 2.79         |

\*Measured at 1 atm.

as NaCl or CaCl<sub>2</sub>. This method of thawing succeeds because it depresses the freezing point of water.

Figure 13.7 shows that lowering the vapor pressure of the solution shifts the solid-liquid curve to the left. Consequently, this line intersects the horizontal line at a temperature *lower* than the freezing point of water. The *freezing-point depression*,  $\Delta T_f$ , is defined as

$$\Delta T_f = T_f^\circ - T_f$$

in which  $T_f^\circ$  is the freezing point of the pure solvent, and  $T_f$  the freezing point of the solution. Again,  $\Delta T_f$  is proportional to the concentration of the solution:

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m \quad (13.9)$$

in which  $m$  is the concentration of the solute in molality units, and  $K_f$  is the *molal freezing-point depression constant* (see Table 13.2). Like  $K_b$ ,  $K_f$  has the units °C/m.

A qualitative explanation of the freezing-point depression phenomenon is as follows. Freezing involves a transition from the disordered state to the ordered state. For this to happen, energy must be removed from the system. Because a solution has greater disorder than the solvent, more energy needs to be removed from it to create order than in the case of a pure solvent. Therefore, the solution has a lower freezing point than the solvent. Note that when a solution freezes, the solid that separates is the solvent component.

Whereas the solute must be nonvolatile in the case of boiling-point elevation, no such restriction applies to freezing-point depression. For example, methanol (CH<sub>3</sub>OH), a fairly volatile liquid that boils at only 65°C, has sometimes been used as an antifreeze in automobile radiators.

### Example 13.7

Ethylene glycol (EG), CH<sub>2</sub>(OH)CH<sub>2</sub>(OH), is a common automobile antifreeze. It is water soluble and fairly nonvolatile (b.p. 197°C). Calculate the freezing point of a solution containing 651 g of this substance in 2505 g of water. Would you keep this substance in your car radiator during the summer? The molar mass of ethylene glycol is 62.01 g.

(Continued)



In cold climate regions, antifreeze must be used in car radiators in winter.

**Strategy** This question asks for the depression in freezing point of the solution.

$$\Delta T_f = K_f m$$

want to calculate      constant  
                                ↑  
                                need to find

The information given enables us to calculate the molality of the solution and we refer to Table 13.2 for the  $K_f$  of water.

**Solution** To solve for the molality of the solution, we need to know the number of moles of EG and the mass of the solvent in kilograms. We find the molar mass of EG, and convert the mass of the solvent to 2.505 kg, and calculate the molality as follows:

$$\begin{aligned} 651 \text{ g EG} &\times \frac{1 \text{ mol EG}}{62.07 \text{ g EG}} = 10.5 \text{ mol EG} \\ \text{molality} &= \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} \\ &= \frac{10.5 \text{ mol EG}}{2.505 \text{ kg H}_2\text{O}} = 4.19 \text{ mol EG/kg H}_2\text{O} \\ &= 4.19 \text{ m} \end{aligned}$$

From Equation (13.9) and Table 13.2 we write

$$\begin{aligned} \Delta T_f &= K_f m \\ &= (1.86^\circ\text{C}/m)(4.19 \text{ m}) \\ &= 7.79^\circ\text{C} \end{aligned}$$

Because pure water freezes at  $0^\circ\text{C}$ , the solution will freeze at  $-7.79^\circ\text{C}$ . We can calculate boiling-point elevation in the same way as follows:

$$\begin{aligned} \Delta T_b &= K_b m \\ &= (0.52^\circ\text{C}/m)(4.19 \text{ m}) \\ &= 2.2^\circ\text{C} \end{aligned}$$

Because the solution will boil at  $(100 + 2.2)^\circ\text{C}$ , or  $102.2^\circ\text{C}$ , it would be preferable to leave the antifreeze in your car radiator in summer to prevent the solution from boiling.

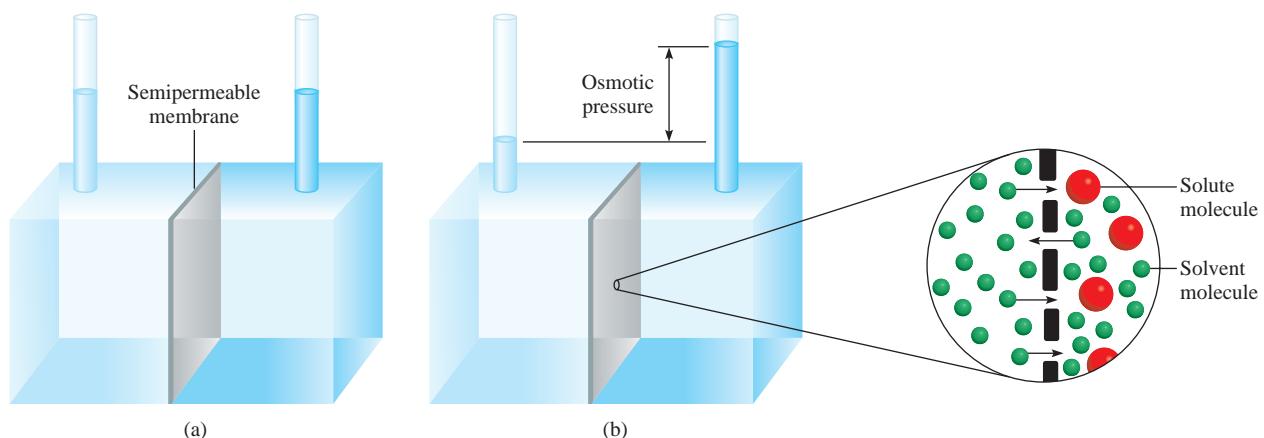
**Similar problems:** 13.56, 13.59.

**Practice Exercise** Calculate the boiling point and freezing point of a solution containing 478 g of ethylene glycol in 3202 g of water.



## Osmotic Pressure

Many chemical and biological processes depend on the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one. Figure 13.8 illustrates this phenomenon. The left compartment of the apparatus contains pure solvent; the right compartment contains a solution. The two compartments are separated by a **semipermeable membrane**, which *allows solvent molecules to pass through but blocks the passage of solute molecules*. At the start, the water levels in the two tubes are equal [see Figure 13.8(a)]. After some time, the level in the right tube begins to rise; this continues until equilibrium is reached. *The net movement of solvent molecules through a semipermeable membrane from a pure solvent or from a dilute solution to a more concentrated solution is called osmosis.* The **osmotic pressure ( $\pi$ )** of a solution is *the pressure required to stop osmosis*. As shown in Figure 13.8(b), this pressure can be measured directly from the difference in the final fluid levels.

**Figure 13.8**

Osmotic pressure. (a) The levels of the pure solvent (left) and of the solution (right) are equal at the start. (b) During osmosis, the level on the solution side rises as a result of the net flow of solvent from left to right. The osmotic pressure is equal to the hydrostatic pressure exerted by the column of fluid in the right tube at equilibrium. Basically the same effect occurs when the pure solvent is replaced by a more dilute solution than that on the right.

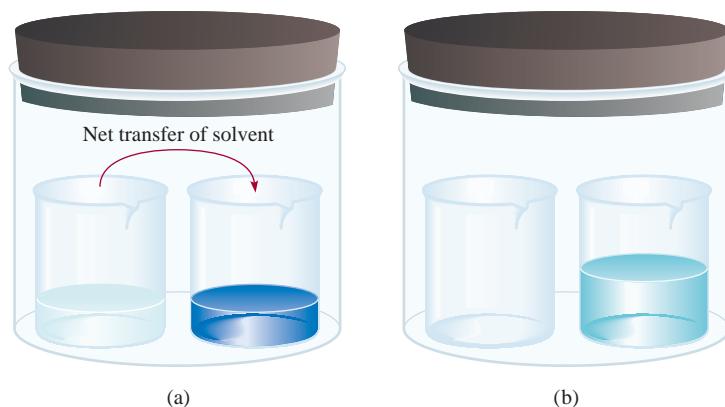
What causes water to move spontaneously from left to right in this case? Compare the vapor pressure of pure water and that of water from a solution (Figure 13.9). Because the vapor pressure of pure water is higher, there is a net transfer of water from the left beaker to the right one. Given enough time, the transfer will continue to completion. A similar force causes water to move into the solution during osmosis.

Although osmosis is a common and well-studied phenomenon, relatively little is known about how the semipermeable membrane stops some molecules yet allows others to pass. In some cases, it is simply a matter of size. A semipermeable membrane may have pores small enough to let only the solvent molecules through. In other cases, a different mechanism may be responsible for the membrane's selectivity—for example, the solvent's greater "solubility" in the membrane.

The osmotic pressure of a solution is given by

$$\pi = MRT \quad (13.10)$$

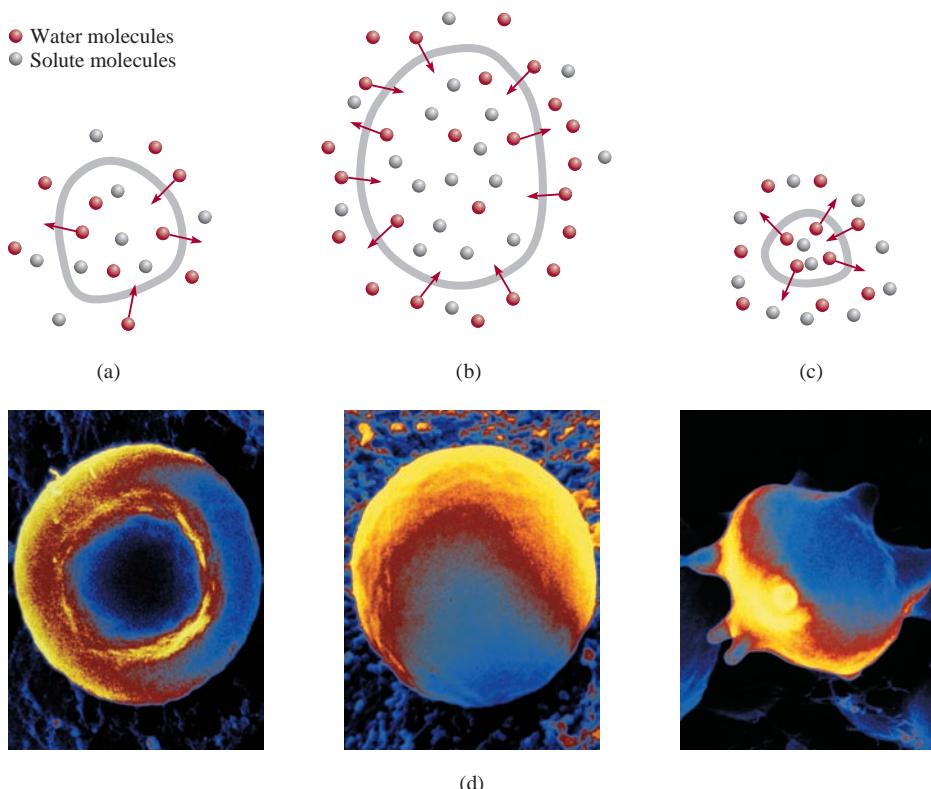
in which  $M$  is the molarity of solution,  $R$  is the gas constant ( $0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol}$ ), and  $T$  is the absolute temperature. The osmotic pressure,  $\pi$ , is expressed in atmospheres.

**Figure 13.9**

(a) Unequal vapor pressures inside the container lead to a net transfer of water from the left beaker (which contains pure water) to the right one (which contains a solution). (b) At equilibrium, all the water in the left beaker has been transferred to the right beaker. This driving force for solvent transfer is analogous to the osmotic phenomenon that is shown in Figure 13.8.

**Figure 13.10**

A cell in (a) an isotonic solution, (b) a hypotonic solution, and (c) a hypertonic solution. The cell remains unchanged in (a), swells in (b), and shrinks in (c). (d) From left to right: a red blood cell in an isotonic solution, in a hypotonic solution, and in a hypertonic solution.



Because osmotic pressure measurements are carried out at constant temperature, we express the concentration here in terms of the more convenient units of molarity rather than molality.

Like boiling-point elevation and freezing-point depression, osmotic pressure is directly proportional to the concentration of solution. This is what we would expect, bearing in mind that all colligative properties depend only on the number of solute particles in solution. If two solutions are of equal concentration and, hence, of the same osmotic pressure, they are said to be *isotonic*. If two solutions are of unequal osmotic pressures, the more concentrated solution is said to be *hypertonic* and the more dilute solution is described as *hypotonic* (Figure 13.10).

The osmotic pressure phenomenon manifests itself in many interesting applications. To study the contents of red blood cells, which are protected from the external environment by a semipermeable membrane, biochemists use a technique called hemolysis. The red blood cells are placed in a hypotonic solution. Because the hypotonic solution is less concentrated than the interior of the cell, water moves into the cells, as shown in Figure 13.10(b). The cells swell and eventually burst, releasing hemoglobin and other molecules.

Home preserving of jam and jelly provides another example of the use of osmotic pressure. A large quantity of sugar is actually essential to the preservation process because the sugar helps to kill bacteria that may cause botulism. As Figure 13.10(c) shows, when a bacterial cell is in a hypertonic (high-concentration) sugar solution, the intracellular water tends to move out of the bacterial cell to the more concentrated solution by osmosis. This process, known as *crenulation*, causes the cell to shrink and, eventually, to cease functioning. The natural acidity of fruits also inhibits bacterial growth.

Osmotic pressure also is the major mechanism for transporting water upward in plants. Because leaves constantly lose water to the air, in a process called *transpiration*, the solute concentrations in leaf fluids increase. Water is pushed up through the trunk, branches, and stems of trees by osmotic pressure. Up to 10 to 15 atm pressure is necessary to transport water to the leaves at the tops of California's redwoods, which reach about 120 m in height. (The capillary action discussed in Section 12.3 is responsible for the rise of water only up to a few centimeters.)



California redwoods.

## Using Colligative Properties to Determine Molar Mass

The colligative properties of nonelectrolyte solutions provide a means of determining the molar mass of a solute. Theoretically, any of the four colligative properties are suitable for this purpose. In practice, however, only freezing-point depression and osmotic pressure are used because they show the most pronounced changes.

### Example 13.8

A 7.85-g sample of a compound with the empirical formula  $C_5H_4$  is dissolved in 301 g of benzene. The freezing point of the solution is  $1.05^{\circ}\text{C}$  below that of pure benzene. What are the molar mass and molecular formula of this compound?

**Strategy** Solving this problem requires three steps. First, we calculate the molality of the solution from the depression in freezing point. Next, from the molality we determine the number of moles in 7.85 g of the compound and hence its molar mass. Finally, comparing the experimental molar mass with the empirical molar mass enables us to write the molecular formula.

**Solution** The sequence of conversions for calculating the molar mass of the compound is



Our first step is to calculate the molality of the solution. From Equation (13.9) and Table 13.2 we write

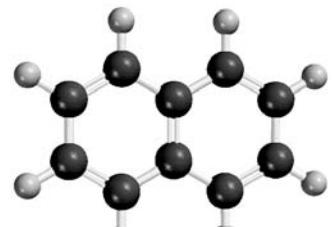
$$\text{molality} = \frac{\Delta T_f}{K_f} = \frac{1.05^{\circ}\text{C}}{5.12^{\circ}\text{C}/\text{mol}} = 0.205 \text{ mol/kg}$$

Because there is 0.205 mole of the solute in 1 kg of solvent, the number of moles of solute in 301 g, or 0.301 kg, of solvent is

$$0.301 \text{ kg} \times \frac{0.205 \text{ mol}}{1 \text{ kg}} = 0.0617 \text{ mol}$$

Thus, the molar mass of the solute is

$$\begin{aligned} \text{molar mass} &= \frac{\text{grams of compound}}{\text{moles of compound}} \\ &= \frac{7.85 \text{ g}}{0.0617 \text{ mol}} = 127 \text{ g/mol} \end{aligned}$$



(Continued)

Now we can determine the ratio

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{127 \text{ g/mol}}{64 \text{ g/mol}} \approx 2$$

**Similar problem:** 13.57.

Therefore, the molecular formula is  $(\text{C}_5\text{H}_4)_2$  or  $\text{C}_{10}\text{H}_8$  (naphthalene).

**Practice Exercise** A solution of 0.85 g of an organic compound in 100.0 g of benzene has a freezing point of  $5.16^\circ\text{C}$ . What are the molality of the solution and the molar mass of the solute?

### Example 13.9

A solution is prepared by dissolving 35.0 g of hemoglobin (Hb) in enough water to make up 1 L in volume. If the osmotic pressure of the solution is found to be 10.0 mmHg at  $25^\circ\text{C}$ , calculate the molar mass of hemoglobin.

**Strategy** We are asked to calculate the molar mass of Hb. The steps are similar to those outlined in Example 13.8. From the osmotic pressure of the solution, we calculate the molarity of the solution. Then, from the molarity, we determine the number of moles in 35.0 g of Hb and hence its molar mass. What units should we use for  $\pi$  and temperature?

**Solution** The sequence of conversions is as follows:



First we calculate the molarity using Equation (13.10)

$$\pi = MRT$$

$$\begin{aligned} M &= \frac{\pi}{RT} \\ &= \frac{10.0 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})} \\ &= 5.38 \times 10^{-4} \text{ M} \end{aligned}$$

The volume of the solution is 1 L, so it must contain  $5.38 \times 10^{-4}$  mole of Hb. We use this quantity to calculate the molar mass:

$$\begin{aligned} \text{moles of Hb} &= \frac{\text{mass of Hb}}{\text{molar mass of Hb}} \\ \text{molar mass of Hb} &= \frac{\text{mass of Hb}}{\text{moles of Hb}} \\ &= \frac{35.0 \text{ g}}{5.38 \times 10^{-4} \text{ mol}} \\ &= 6.51 \times 10^4 \text{ g/mol} \end{aligned}$$

**Similar problems:** 13.64, 13.66.

**Practice Exercise** A 202-mL benzene solution containing 2.47 g of an organic polymer has an osmotic pressure of 8.63 mmHg at  $21^\circ\text{C}$ . Calculate the molar mass of the polymer.

A pressure of 10.0 mmHg, as in Example 13.9, can be measured easily and accurately. For this reason, osmotic pressure measurements are very useful for determining the molar masses of large molecules, such as proteins. To see how much more practical the osmotic pressure technique is than freezing-point depression would be, let us estimate the change in freezing point of the same hemoglobin solution. If an aqueous solution is quite dilute, we can assume that molarity is roughly equal to molality. (Molarity would be equal to molality if the density of the aqueous solution were 1 g/mL.) Hence, from Equation (13.9) we write

$$\begin{aligned}\Delta T_f &= (1.86^\circ\text{C}/m)(5.38 \times 10^{-4} \text{ m}) \\ &= 1.00 \times 10^{-3}^\circ\text{C}\end{aligned}$$

The freezing-point depression of one-thousandth of a degree is too small a temperature change to measure accurately. For this reason, the freezing-point depression technique is more suitable for determining the molar mass of smaller and more soluble molecules, those having molar masses of 500 g or less, because the freezing-point depressions of their solutions are much greater.

The density of mercury is 13.6 g/mL. Therefore, 10 mmHg corresponds to a column of water 13.6 cm in height.

## Colligative Properties of Electrolyte Solutions

The colligative properties of electrolytes require a slightly different approach than the one used for the colligative properties of nonelectrolytes. The reason is that electrolytes dissociate into ions in solution, and so one unit of an electrolyte compound separates into two or more particles when it dissolves. (Remember, it is the number of solute particles that determines the colligative properties of a solution.) For example, each unit of NaCl dissociates into two ions— $\text{Na}^+$  and  $\text{Cl}^-$ . Thus, the colligative properties of a 0.1 *m* NaCl solution should be twice as great as those of a 0.1 *m* solution containing a nonelectrolyte, such as sucrose. Similarly, we would expect a 0.1 *m* CaCl<sub>2</sub> solution to depress the freezing point by three times as much as a 0.1 *m* sucrose solution. To account for this effect we must modify the equations for colligative properties as follows:

$$\Delta T_b = iK_b m \quad (13.11)$$

$$\Delta T_f = iK_f m \quad (13.12)$$

$$\pi = iMRT \quad (13.13)$$

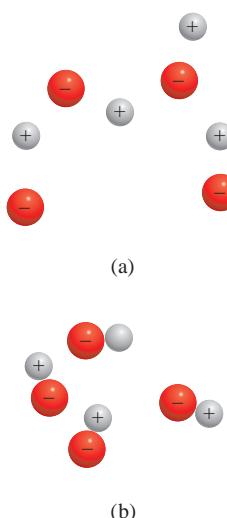


**Interactivity:**  
Test Solution with Electrolytes  
ARIS, Interactives

The variable *i* is the *van't Hoff factor*, which is defined as

$$i = \frac{\text{actual number of particles in soln after dissociation}}{\text{number of formula units initially dissolved in soln}} \quad (13.14)$$

Thus, *i* should be 1 for all nonelectrolytes. For strong electrolytes such as NaCl and KNO<sub>3</sub>, *i* should be 2, and for strong electrolytes such as Na<sub>2</sub>SO<sub>4</sub> and MgCl<sub>2</sub>, *i* should be 3.

**Figure 13.11**

(a) Free ions and (b) ion pairs in solution. Such an ion pair bears no net charge and therefore cannot conduct electricity in solution.

**TABLE 13.3****The van't Hoff Factor of 0.0500 M Electrolyte Solutions at 25°C**

| Electrolyte       | <i>i</i> (measured) | <i>i</i> (calculated) |
|-------------------|---------------------|-----------------------|
| Sucrose*          | 1.0                 | 1.0                   |
| HCl               | 1.9                 | 2.0                   |
| NaCl              | 1.9                 | 2.0                   |
| MgSO <sub>4</sub> | 1.3                 | 2.0                   |
| MgCl <sub>2</sub> | 2.7                 | 3.0                   |
| FeCl <sub>3</sub> | 3.4                 | 4.0                   |

\*Sucrose is a nonelectrolyte. It is listed here for comparison only.

In reality, the colligative properties of electrolyte solutions are usually smaller than anticipated because at higher concentrations, electrostatic forces come into play, drawing cations and anions together. A cation and an anion held together by electrostatic forces is called an **ion pair**. The formation of an ion pair reduces the number of particles in solution by one, causing a reduction in the colligative properties (Figure 13.11). Table 13.3 shows the experimentally measured values of *i* and those calculated assuming complete dissociation. As you can see, the agreement is close but not perfect, indicating that the extent of ion-pair formation in these solutions is appreciable.

**Example 13.10**

The osmotic pressure of a 0.010 M potassium iodide (KI) solution at 25°C is 0.465 atm. Calculate the van't Hoff factor for KI at this concentration.

**Strategy** Note that KI is a strong electrolyte, so we expect it to dissociate completely in solution. If so, its osmotic pressure would be

$$2(0.010 \text{ M})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K}) = 0.489 \text{ atm}$$

However, the measured osmotic pressure is only 0.465 atm. The smaller than predicted osmotic pressure means that there is ion-pair formation, which reduces the number of solute particles (K<sup>+</sup> and I<sup>-</sup> ions) in solution.

**Solution** From Equation (13.13) we have

$$\begin{aligned} i &= \frac{\pi}{MRT} \\ &= \frac{0.465 \text{ atm}}{(0.010 \text{ M})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})} \\ &= 1.90 \end{aligned}$$

Similar problem: 13.79.

**Practice Exercise** The freezing-point depression of a 0.100 m MgSO<sub>4</sub> solution is 0.225°C. Calculate the van't Hoff factor of MgSO<sub>4</sub> at this concentration.

## KEY EQUATIONS

|   |         |   |
|---|---------|---|
| $\text{molality } (m) = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$   | (13.4)  | Calculating the molality of a solution.   |
| $c = kP$  | (13.5)  | Henry's law for calculating solubility of gases.  |
| $P_1 = X_1 P_1^\circ$   | (13.6)  | Raoult's law relating the vapor pressure of a liquid to its vapor pressure in a solution. |
| $\Delta P = X_2 P_1^\circ$  | (13.7)  | Vapor pressure lowering in terms of the concentration of solution.                        |
| $\Delta T_b = K_b m$  | (13.8)  | Boiling-point elevation.  |
| $\Delta T_f = K_f m$  | (13.9)  | Freezing-point depression.  |
| $\pi = MRT$   | (13.10) | Osmotic pressure of a solution.   |
| $i = \frac{\text{actual number of particles in soln after dissociation}}{\text{number of formula units initially dissolved in soln}}$ | (13.14) | Calculating the van't Hoff factor for an electrolyte solution.                            |

## SUMMARY OF FACTS AND CONCEPTS

1. Solutions are homogeneous mixtures of two or more substances, which may be solids, liquids, or gases. The ease of dissolution of a solute in a solvent is governed by intermolecular forces. Energy and the increase in disorder that result when molecules of the solute and solvent mix to form a solution are the forces driving the solution process.
2. The concentration of a solution can be expressed as percent by mass, mole fraction, molarity, and molality. The circumstances dictate which units are appropriate.
3. A rise in temperature usually increases the solubility of solid and liquid substances and decreases the solubility of gases. According to Henry's law, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas over the solution.
4. Raoult's law states that the partial pressure of a substance A over a solution is related to the mole fraction ( $X_A$ ) of A and to the vapor pressure ( $P_A^\circ$ ) of pure A as:  $P_A = X_A P_A^\circ$ . An ideal solution obeys Raoult's law over the entire range of concentration. In practice, very few solutions exhibit ideal behavior.
5. Vapor-pressure lowering, boiling-point elevation, freezing-point depression, and osmotic pressure are colligative properties of solutions; that is, they are properties that depend only on the number of solute particles that are present and not on their nature. In electrolyte solutions, the interaction between ions leads to the formation of ion pairs. The van't Hoff factor provides a measure of the extent of ion-pair formation in solution.

## KEY WORDS

|                                |                                    |                                |                                 |
|--------------------------------|------------------------------------|--------------------------------|---------------------------------|
| Colligative properties, p. 435 | Miscible, p. 428                   | Percent by mass, p. 429        | Solvation, p. 428               |
| Crystallization, p. 426        | Molality, p. 429                   | Raoult's law, p. 435           | Supersaturated solution, p. 426 |
| Henry's law, p. 433            | Nonvolatile, p. 435                | Saturated solution, p. 426     | Thermal pollution, p. 432       |
| Ideal solution, p. 437         | Osmosis, p. 440                    | Semipermeable membrane, p. 440 | Unsaturated solution, p. 426    |
| Ion pair, p. 446               | Osmotic pressure ( $\pi$ ), p. 440 |                                | Volatile, p. 437                |

## QUESTIONS AND PROBLEMS

### The Solution Process

#### Review Questions

- 13.1 Briefly describe the solution process at the molecular level. Use the dissolution of a solid in a liquid as an example.
- 13.2 Basing your answer on intermolecular force considerations, explain what “like dissolves like” means.
- 13.3 What is solvation? What are the factors that influence the extent to which solvation occurs? Give two examples of solvation, including one that involves ion-dipole interaction and another in which dispersion forces come into play.
- 13.4 As you know, some solution processes are endothermic and others are exothermic. Provide a molecular interpretation for the difference.
- 13.5 Explain why the solution process invariably leads to an increase in disorder.
- 13.6 Describe the factors that affect the solubility of a solid in a liquid. What does it mean to say that two liquids are miscible?

#### Problems

- 13.7 Why is naphthalene ( $C_{10}H_8$ ) more soluble than CsF in benzene?
- 13.8** Explain why ethanol ( $C_2H_5OH$ ) is not soluble in cyclohexane ( $C_6H_{12}$ ).
- 13.9 Arrange these compounds in order of increasing solubility in water:  $O_2$ ,  $LiCl$ ,  $Br_2$ ,  $CH_3OH$  (methanol).
- 13.10** Explain the variations in solubility in water of the alcohols listed here:

| Compound                 | Solubility in Water<br>g/100 g, 20°C |
|--------------------------|--------------------------------------|
| $CH_3OH$                 | $\infty$                             |
| $CH_3CH_2OH$             | $\infty$                             |
| $CH_3CH_2CH_2OH$         | $\infty$                             |
| $CH_3CH_2CH_2CH_2OH$     | 9                                    |
| $CH_3CH_2CH_2CH_2CH_2OH$ | 2.7                                  |

*Note:*  $\infty$  means the alcohol and water are completely miscible in all proportions.

### Concentration Units

#### Review Questions

- 13.11 Define these concentration terms and give their units: percent by mass, molarity, molality. Compare their advantages and disadvantages.

- 13.12 Outline the steps required for conversion among molarity, molality, and percent by mass.

#### Problems

- 13.13 Calculate the percent by mass of the solute in each of these aqueous solutions: (a) 5.50 g of NaBr in 78.2 g of solution, (b) 31.0 g of KCl in 152 g of water, (c) 4.5 g of toluene in 29 g of benzene.
- 13.14** Calculate the amount of water (in grams) that must be added to (a) 5.00 g of urea  $[(NH_2)_2CO]$  in the preparation of a 16.2 percent by mass solution and (b) 26.2 g of  $MgCl_2$  in the preparation of a 1.5 percent by mass solution.
- 13.15 Calculate the molality of each of these solutions: (a) 14.3 g of sucrose ( $C_{12}H_{22}O_{11}$ ) in 676 g of water, (b) 7.20 moles of ethylene glycol ( $C_2H_6O_2$ ) in 3546 g of water.
- 13.16** Calculate the molality of each of the following aqueous solutions: (a) 2.50 M NaCl solution (density of solution = 1.08 g/mL), (b) 48.2 percent by mass KBr solution.
- 13.17 Calculate the molalities of these aqueous solutions: (a) 1.22 M sugar ( $C_{12}H_{22}O_{11}$ ) solution (density of solution = 1.12 g/mL), (b) 0.87 M NaOH solution (density of solution = 1.04 g/mL), (c) 5.24 M  $NaHCO_3$  solution (density of solution = 1.19 g/mL).
- 13.18** For dilute aqueous solutions in which the density of the solution is roughly equal to that of the pure solvent, the molarity of the solution is equal to its molality. Show that this statement is correct for a 0.010 M urea  $[(NH_2)_2CO]$  solution.
- 13.19 The alcohol content of hard liquor is normally given in terms of the “proof,” which is defined as twice the percentage by volume of ethanol ( $C_2H_5OH$ ) present. Calculate the number of grams of alcohol present in 1.00 L of 75 proof gin. The density of ethanol is 0.798 g/mL.
- 13.20** The concentrated sulfuric acid we use in the laboratory is 98.0 percent  $H_2SO_4$  by mass. Calculate the molality and molarity of the acid solution. The density of the solution is 1.83 g/mL.
- 13.21 Calculate the molarity and the molality of  $NH_3$  for a solution of 30.0 g of  $NH_3$  in 70.0 g of water. The density of the solution is 0.982 g/mL.
- 13.22** The density of an aqueous solution containing 10.0 percent ethanol ( $C_2H_5OH$ ) by mass is 0.984 g/mL. (a) Calculate the molality of this solution. (b) Calculate its molarity. (c) What volume of the solution would contain 0.125 mole of ethanol?

## Effect of Temperature and Pressure on Solubility

### Review Questions

- 13.23 How do the solubilities of most ionic compounds in water change with temperature?
- 13.24 What is the effect of pressure on the solubility of a liquid in liquid and of a solid in liquid?

### Problems

- 13.25 A 3.20-g sample of a salt dissolves in 9.10 g of water to give a saturated solution at 25°C. What is the solubility (in g salt/100 g of H<sub>2</sub>O) of the salt?
- 13.26** The solubility of KNO<sub>3</sub> is 155 g per 100 g of water at 75°C and 38.0 g at 25°C. What mass (in grams) of KNO<sub>3</sub> will crystallize out of solution if exactly 100 g of its saturated solution at 75°C are cooled to 25°C?

## Gas Solubility

### Review Questions

- 13.27 Discuss the factors that influence the solubility of a gas in a liquid. Explain why the solubility of a gas in a liquid usually decreases with increasing temperature.
- 13.28 What is thermal pollution? Why is it harmful to aquatic life?
- 13.29 What is Henry's law? Define each term in the equation, and give its units. Explain the law in terms of the kinetic molecular theory of gases.
- 13.30 Give two exceptions to Henry's law.

### Problems

- 13.31 A student is observing two beakers of water. One beaker is heated to 30°C, and the other is heated to 100°C. In each case, bubbles form in the water. Are these bubbles of the same origin? Explain.
- 13.32** A man bought a goldfish in a pet shop. Upon returning home, he put the goldfish in a bowl of recently boiled water that had been cooled quickly. A few minutes later the fish was dead. Explain what happened to the fish.
- 13.33 A beaker of water is initially saturated with dissolved air. Explain what happens when He gas at 1 atm is bubbled through the solution for a long time.
- 13.34** A miner working 260 m below sea level opened a carbonated soft drink during a lunch break. To his surprise, the soft drink tasted rather "flat." Shortly afterward, the miner took an elevator to the surface. During the trip up, he could not stop belching. Why?
- 13.35 The solubility of CO<sub>2</sub> in water at 25°C and 1 atm is 0.034 mol/L. What is its solubility under atmos-

pheric conditions? (The partial pressure of CO<sub>2</sub> in air is 0.0003 atm.) Assume that CO<sub>2</sub> obeys Henry's law.

- 13.36** The solubility of N<sub>2</sub> in blood at 37°C and at a partial pressure of 0.80 atm is  $5.6 \times 10^{-4}$  mol/L. A deep-sea diver breathes compressed air with the partial pressure of N<sub>2</sub> equal to 4.0 atm. Assume that the total volume of blood in the body is 5.0 L. Calculate the amount of N<sub>2</sub> gas released (in liters) when the diver returns to the surface of the water, where the partial pressure of N<sub>2</sub> is 0.80 atm.

## Colligative Properties of Nonelectrolyte Solutions

### Review Questions

- 13.37 What are colligative properties? What is the meaning of the word "colligative" in this context?
- 13.38 Give two examples of a volatile liquid and two examples of a nonvolatile liquid.
- 13.39 Define Raoult's law. Define each term in the equation representing Raoult's law, and give its units. What is an ideal solution?
- 13.40 Define boiling-point elevation and freezing-point depression. Write the equations relating boiling-point elevation and freezing-point depression to the concentration of the solution. Define all the terms, and give their units.
- 13.41 How is the lowering in vapor pressure related to a rise in the boiling point of a solution?
- 13.42 Use a phase diagram to show the difference in freezing point and boiling point between an aqueous urea solution and pure water.
- 13.43 What is osmosis? What is a semipermeable membrane?
- 13.44 Write the equation relating osmotic pressure to the concentration of a solution. Define all the terms and give their units.
- 13.45 What does it mean when we say that the osmotic pressure of a sample of seawater is 25 atm at a certain temperature?
- 13.46 Explain why molality is used for boiling-point elevation and freezing-point depression calculations and molarity is used in osmotic pressure calculations.
- 13.47 Describe how you would use the freezing-point depression and osmotic pressure measurements to determine the molar mass of a compound. Why is the boiling-point elevation phenomenon normally not used for this purpose?
- 13.48 Explain why it is essential that fluids used in intravenous injections have approximately the same osmotic pressure as blood.

### Problems

- 13.49 A solution is prepared by dissolving 396 g of sucrose ( $C_{12}H_{22}O_{11}$ ) in 624 g of water. What is the vapor pressure of this solution at 30°C? (The vapor pressure of water is 31.8 mmHg at 30°C.)
- 13.50** How many grams of sucrose ( $C_{12}H_{22}O_{11}$ ) must be added to 552 g of water to give a solution with a vapor pressure 2.0 mmHg less than that of pure water at 20°C? (The vapor pressure of water at 20°C is 17.5 mmHg.)
- 13.51 The vapor pressure of benzene is 100.0 mmHg at 26.1°C. Calculate the vapor pressure of a solution containing 24.6 g of camphor ( $C_{10}H_{16}O$ ) dissolved in 98.5 g of benzene. (Camphor is a low-volatility solid.)
- 13.52** The vapor pressures of ethanol ( $C_2H_5OH$ ) and 1-propanol ( $C_3H_7OH$ ) at 35°C are 100 mmHg and 37.6 mmHg, respectively. Assume ideal behavior and calculate the partial pressures of ethanol and 1-propanol at 35°C over a solution of ethanol in 1-propanol, in which the mole fraction of ethanol is 0.300.
- 13.53 The vapor pressure of ethanol ( $C_2H_5OH$ ) at 20°C is 44 mmHg, and the vapor pressure of methanol ( $CH_3OH$ ) at the same temperature is 94 mmHg. A mixture of 30.0 g of methanol and 45.0 g of ethanol is prepared (and may be assumed to behave as an ideal solution). (a) Calculate the vapor pressure of methanol and ethanol above this solution at 20°C. (b) Calculate the mole fraction of methanol and ethanol in the vapor above this solution at 20°C.
- 13.54** How many grams of urea [ $(NH_2)_2CO$ ] must be added to 450 g of water to give a solution with a vapor pressure 2.50 mmHg less than that of pure water at 30°C? (The vapor pressure of water at 30°C is 31.8 mmHg.)
- 13.55 What are the boiling point and freezing point of a 2.47 *m* solution of naphthalene in benzene? (The boiling point and freezing point of benzene are 80.1°C and 5.5°C, respectively.)
- 13.56** An aqueous solution contains the amino acid glycine ( $NH_2CH_2COOH$ ). Assuming no ionization of the acid, calculate the molality of the solution if it freezes at -1.1°C.
- 13.57 Pheromones are compounds secreted by the females of many insect species to attract males. One of these compounds contains 80.78% C, 13.56% H, and 5.66% O. A solution of 1.00 g of this pheromone in 8.50 g of benzene freezes at 3.37°C. What are the molecular formula and molar mass of the compound? (The normal freezing point of pure benzene is 5.50°C).
- 13.58** The elemental analysis of an organic solid extracted from gum arabic showed that it contained 40.0% C, 6.7% H, and 53.3% O. A solution of 0.650 g of the solid in 27.8 g of the solvent diphenyl gave a freezing-point depression of 1.56°C. Calculate the molar mass and molecular formula of the solid. ( $K_f$  for diphenyl is 8.00°C/m.)
- 13.59 How many liters of the antifreeze ethylene glycol [ $CH_2(OH)CH_2(OH)$ ] would you add to a car radiator containing 6.50 L of water if the coldest winter temperature in your area is -20°C? Calculate the boiling point of this water-ethylene glycol mixture. The density of ethylene glycol is 1.11 g/mL.
- 13.60** A solution is prepared by condensing 4.00 L of a gas, measured at 27°C and 748 mmHg pressure, into 58.0 g of benzene. Calculate the freezing point of this solution.
- 13.61 The molar mass of benzoic acid ( $C_6H_5COOH$ ) determined by measuring the freezing-point depression in benzene is twice that expected for the molecular formula,  $C_7H_6O_2$ . Explain this apparent anomaly.
- 13.62** A solution of 2.50 g of a compound of empirical formula  $C_6H_5P$  in 25.0 g of benzene is observed to freeze at 4.3°C. Calculate the molar mass of the solute and its molecular formula.
- 13.63 What is the osmotic pressure (in atmospheres) of a 12.36 M aqueous urea solution at 22.0°C?
- 13.64** A solution containing 0.8330 g of a protein of unknown structure in 170.0 mL of aqueous solution was found to have an osmotic pressure of 5.20 mmHg at 25°C. Determine the molar mass of the protein.
- 13.65 A quantity of 7.480 g of an organic compound is dissolved in water to make 300.0 mL of solution. The solution has an osmotic pressure of 1.43 atm at 27°C. The analysis of this compound shows it to contain 41.8% C, 4.7% H, 37.3% O, and 16.3% N. Calculate the molecular formula of the organic compound.
- 13.66** A solution of 6.85 g of a carbohydrate in 100.0 g of water has a density of 1.024 g/mL and an osmotic pressure of 4.61 atm at 20.0°C. Calculate the molar mass of the carbohydrate.

### Colligative Properties of Electrolyte Solutions

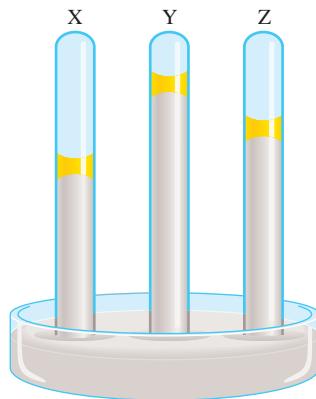
#### Review Questions

- 13.67 Why is the discussion of the colligative properties of electrolyte solutions more involved than that of non-electrolyte solutions?
- 13.68 Define ion pairs. What effect does ion-pair formation have on the colligative properties of a solution? How does the ease of ion-pair formation depend on (a) charges on the ions, (b) size of the ions, (c) nature of the solvent (polar versus nonpolar), (d) concentration?

- 13.69 In each case, indicate which of these pairs of compounds is more likely to form ion pairs in water: (a) NaCl or Na<sub>2</sub>SO<sub>4</sub>, (b) MgCl<sub>2</sub> or MgSO<sub>4</sub>, (c) LiBr or KBr.
- 13.70 Define the van't Hoff factor. What information does this quantity provide?

### Problems

- 13.71 Which of these two aqueous solutions has (a) the higher boiling point, (b) the higher freezing point, and (c) the lower vapor pressure: 0.35 *m* CaCl<sub>2</sub> or 0.90 *m* urea? State your reasons.
- 13.72** Consider two aqueous solutions, one of sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) and the other of nitric acid (HNO<sub>3</sub>), both of which freeze at -1.5°C. What other properties do these solutions have in common?
- 13.73 Arrange these solutions in order of decreasing freezing point: (a) 0.10 *m* Na<sub>3</sub>PO<sub>4</sub>, (b) 0.35 *m* NaCl, (c) 0.20 *m* MgCl<sub>2</sub>, (d) 0.15 *m* C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, (e) 0.15 *m* CH<sub>3</sub>COOH.
- 13.74** Arrange these aqueous solutions in order of decreasing freezing point and explain your reasons: (a) 0.50 *m* HCl, (b) 0.50 *m* glucose, (c) 0.50 *m* acetic acid.
- 13.75 What are the normal freezing points and boiling points of the following solutions: (a) 21.2 g NaCl in 135 mL of water, (b) 15.4 g of urea in 66.7 mL of water?
- 13.76** At 25°C the vapor pressure of pure water is 23.76 mmHg and that of seawater is 22.98 mmHg. Assuming that seawater contains only NaCl, estimate its concentration in molality units.
- 13.77 Both NaCl and CaCl<sub>2</sub> are used to melt ice on roads in winter. What advantages do these substances have over sucrose or urea in lowering the freezing point of water?
- 13.78** A 0.86 percent by mass solution of NaCl is called "physiological saline" because its osmotic pressure is equal to that of the solution in blood cells. Calculate the osmotic pressure of this solution at normal body temperature (37°C). Note that the density of the saline solution is 1.005 g/mL.
- 13.79 The osmotic pressure of 0.010 *M* solutions of CaCl<sub>2</sub> and urea at 25°C are 0.605 atm and 0.245 atm, respectively. Calculate the van't Hoff factor for the CaCl<sub>2</sub> solution.
- 13.80** Calculate the osmotic pressure of a 0.0500 *M* MgSO<sub>4</sub> solution at 22°C. (*Hint:* See Table 13.3.)
- water at 25°C. Calculate the vapor-pressure lowering, the depression in freezing point, the elevation in boiling point, and the osmotic pressure of this solution. (The vapor pressure of water at 25°C = 23.76 mmHg.)
- 13.82** Solutions A and B containing the same solute have osmotic pressures of 2.4 atm and 4.6 atm, respectively, at a certain temperature. What is the osmotic pressure of a solution prepared by mixing equal volumes of A and B at the same temperature?
- 13.83 A cucumber placed in concentrated brine (saltwater) shrivels into a pickle. Explain.
- 13.84** Two liquids A and B have vapor pressures of 76 mmHg and 132 mmHg, respectively, at 25°C. What is the total vapor pressure of the ideal solution made up of (a) 1.00 mole of A and 1.00 mole of B and (b) 2.00 moles of A and 5.00 moles of B?
- 13.85 Calculate the van't Hoff factor of Na<sub>3</sub>PO<sub>4</sub> in a 0.40 *m* aqueous solution whose boiling point is 100.78°C.
- 13.86** A 262-mL sample of a sugar solution containing 1.22 g of the sugar has an osmotic pressure of 30.3 mmHg at 35°C. What is the molar mass of the sugar?
- 13.87 Consider these three mercury manometers. One of them has 1 mL of water placed on top of the mercury, another has 1 mL of a 1 *m* urea solution placed on top of the mercury, and the third one has 1 mL of a 1 *m* NaCl solution placed on top of the mercury. Identify X, Y, and Z with these solutions.

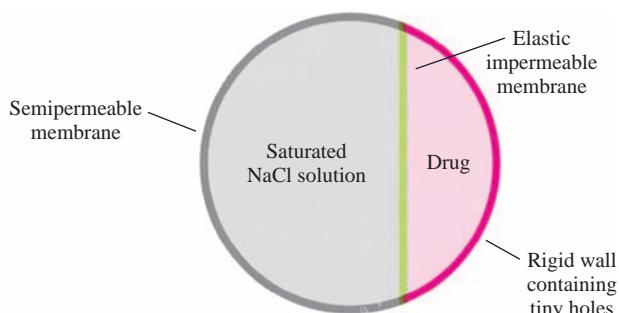


### Additional Problems

- 13.81 Lysozyme is an enzyme that cleaves bacterial cell walls. A sample of lysozyme extracted from chicken egg white has a molar mass of 13,930 g. A quantity of 0.100 g of this enzyme is dissolved in 150 g of

- 13.88 A forensic chemist is given a white powder for analysis. She dissolves 0.50 g of the substance in 8.0 g of benzene. The solution freezes at 3.9°C. Can the chemist conclude that the compound is cocaine (C<sub>17</sub>H<sub>21</sub>NO<sub>4</sub>)? What assumptions are made in the analysis?
- 13.89 "Time-release" drugs have the advantage of releasing the drug to the body at a constant rate so that the drug concentration at any time is not so high as to

have harmful side effects or so low as to be ineffective. A schematic diagram of a pill that works on this basis is shown here. Explain how it works.



- 13.90** Concentrated hydrochloric acid is usually available at 37.7 percent by mass. What is its concentration in molarity? (The density of the solution is 1.19 g/mL.)

- 13.91** A protein has been isolated as a salt with the formula  $\text{Na}_{20}\text{P}$  (this notation means that there are 20  $\text{Na}^+$  ions associated with a negatively charged protein  $\text{P}^{20-}$ ). The osmotic pressure of a 10.0-mL solution containing 0.225 g of the protein is 0.257 atm at 25.0°C. (a) Calculate the molar mass of the protein from these data. (b) What is the actual molar mass of the protein?

- 13.92** A nonvolatile organic compound Z was used to make two solutions. Solution A contains 5.00 g of Z dissolved in 100 g of water, and solution B contains 2.31 g of Z dissolved in 100 g of benzene. Solution A has a vapor pressure of 754.5 mmHg at the normal boiling point of water, and solution B has the same vapor pressure at the normal boiling point of benzene. Calculate the molar mass of Z in solutions A and B and account for the difference.

- 13.93** Hydrogen peroxide with a concentration of 3.0 percent (3.0 g of  $\text{H}_2\text{O}_2$  in 100 mL of solution) is sold in drugstores for use as an antiseptic. For a 10.0-mL 3.0 percent  $\text{H}_2\text{O}_2$  solution, calculate (a) the oxygen gas produced (in liters) at STP when the compound undergoes complete decomposition and (b) the ratio of the volume of  $\text{O}_2$  collected to the initial volume of the  $\text{H}_2\text{O}_2$  solution.

- 13.94** Before a carbonated beverage bottle is sealed, it is pressurized with a mixture of air and carbon dioxide. (a) Explain the effervescence that occurs when the cap of the bottle is removed. (b) What causes the fog to form near the mouth of the bottle right after the cap is removed?

- 13.95** Two beakers, one containing a 50-mL aqueous 1.0 M glucose solution and the other a 50-mL aqueous 2.0 M glucose solution, are placed under a tightly sealed bell jar as that shown in Figure 13.9 at room temperature.

What are the volumes in these two beakers at equilibrium? Assume ideal behavior.

- 13.96** Explain each of these statements: (a) The boiling point of seawater is higher than that of pure water. (b) Carbon dioxide escapes from the solution when the cap is removed from a soft-drink bottle. (c) Molal concentrations and molar concentrations of dilute aqueous solutions are approximately equal. (d) In discussing the colligative properties of a solution (other than osmotic pressure), it is preferable to express the concentration in units of molality rather than in molarity. (e) Methanol (b.p. 65°C) is useful as an auto antifreeze, but it should be removed from the car radiator during the summer season.
- 13.97** Acetic acid is a weak acid that ionizes in solution as follows:



If the freezing point of a 0.106 m  $\text{CH}_3\text{COOH}$  solution is  $-0.203^\circ\text{C}$ , calculate the percent of the acid that has undergone ionization.

- 13.98** A 1.32-g sample of a mixture of cyclohexane ( $\text{C}_6\text{H}_{12}$ ) and naphthalene ( $\text{C}_{10}\text{H}_8$ ) is dissolved in 18.9 g of benzene ( $\text{C}_6\text{H}_6$ ). The freezing point of the solution is  $2.2^\circ\text{C}$ . Calculate the mass percent of the mixture.
- 13.99** How does each of the following affect the solubility of an ionic compound: (a) lattice energy, (b) solvent (polar versus nonpolar), (c) enthalpies of hydration of cation and anion?

- 13.100** A solution contains two volatile liquids A and B. Complete the following table, in which the symbol  $\longleftrightarrow$  indicates attractive intermolecular forces.

| Attractive Forces           | Deviation from Raoult's Law | $\Delta H_{\text{soln}}$ |
|-----------------------------|-----------------------------|--------------------------|
| $A \longleftrightarrow A$ , |                             |                          |
| $B \longleftrightarrow B >$ |                             |                          |
| $A \longleftrightarrow B$   |                             |                          |
|                             | Negative                    |                          |
|                             |                             | Zero                     |

A negative deviation means the vapor pressure of the solution is less than that expected from Raoult's law. The opposite holds for a positive deviation.

- 13.101** A mixture of ethanol and 1-propanol behaves ideally at  $36^\circ\text{C}$  and is in equilibrium with its vapor. If the mole fraction of ethanol in the solution is 0.62, calculate its mole fraction in the vapor phase at this temperature. (The vapor pressures of pure ethanol and 1-propanol at  $36^\circ\text{C}$  are 108 mmHg and 40.0 mmHg, respectively.)

- 13.102** For ideal solutions, the volumes are additive. This means that if 5 mL of A and 5 mL of B form an ideal

solution, the volume of the solution is 10 mL. Provide a molecular interpretation for this observation. When 500 mL of ethanol ( $C_2H_5OH$ ) are mixed with 500 mL of water, the final volume is less than 1000 mL. Why?

- 13.103** Acetic acid is a polar molecule and can form hydrogen bonds with water molecules. Therefore, it has a high solubility in water. Yet acetic acid is also soluble in benzene ( $C_6H_6$ ), a nonpolar solvent that lacks

the ability to form hydrogen bonds. A solution of 3.8 g of  $CH_3COOH$  in 80 g  $C_6H_6$  has a freezing point of  $3.5^\circ C$ . Calculate the molar mass of the solute and explain your result.

- 13.104** A mixture of NaCl and sucrose ( $C_{12}H_{22}O_{11}$ ) of combined mass 10.2 g is dissolved in enough water to make up a 250 mL solution. The osmotic pressure of the solution is 7.32 atm at  $23^\circ C$ . Calculate the mass percent of NaCl in the mixture.

## SPECIAL PROBLEMS

- 13.105** Desalination is a process by which salts are removed from seawater. Three major ways to accomplish desalination are distillation, freezing, and reverse osmosis. The freezing method is based on the fact that when an aqueous solution freezes, the solid that separates from the solution is almost pure water. Reverse osmosis uses water movement from a more concentrated solution to a less concentrated one through a semipermeable membrane.

- With reference to Figure 13.8, draw a diagram showing how reverse osmosis can be carried out.
- What are the advantages and disadvantages of reverse osmosis compared to the freezing and boiling methods?
- What minimum pressure (in atm) must be applied to seawater at  $25^\circ C$  for reverse osmosis to occur? (Treat seawater as an  $0.70\text{ M}$  NaCl solution.)

- 13.106** Liquids A (molar mass 100 g/mol) and B (molar mass 110 g/mol) form an ideal solution. At  $55^\circ C$ , A has a vapor pressure of 95 mmHg and B has a vapor pressure of 42 mmHg. A solution is prepared by mixing equal masses of A and B. (a) Calculate the mole fraction of each component in the solution. (b) Calculate the partial pressures of A and B over the solution at  $55^\circ C$ . (c) Suppose that some of the

vapor described in (b) is condensed to a liquid. Calculate the mole fraction of each component in this liquid and the vapor pressure of each component above this liquid at  $55^\circ C$ .

- 13.107** A very long pipe is capped at one end with a semi-permeable membrane. How deep (in meters) must the pipe be immersed into the sea for fresh water to begin to pass through the membrane? Assume the water to be at  $20^\circ C$  and treat it as a  $0.70\text{ M}$  NaCl solution. The density of seawater is  $1.03\text{ g/cm}^3$  and the acceleration due to gravity is  $9.81\text{ m/s}^2$ .

- 13.108** A mixture of liquids A and B exhibits ideal behavior. At  $84^\circ C$ , the total vapor pressure of a solution containing 1.2 moles of A and 2.3 moles of B is 331 mmHg. Upon the addition of another mole of B to the solution, the vapor pressure increases to 347 mmHg. Calculate the vapor pressures of pure A and B at  $84^\circ C$ .

- 13.109** Using Henry's law and the ideal gas equation to prove the statement that the volume of a gas that dissolves in a given amount of solvent is *independent* of the pressure of the gas. (*Hint:* Henry's law can be modified as  $n = kP$ , where  $n$  is the number of moles of the gas dissolved in the solvent.)

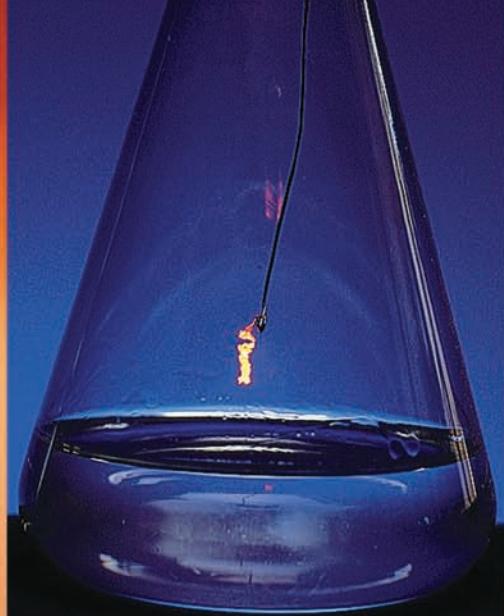
- 13.110** At 298 K, the osmotic pressure of a glucose solution is 10.50 atm. Calculate the freezing point of the solution. The density of the solution is 1.16 g/mL.

## ANSWERS TO PRACTICE EXERCISES

- 13.1** Carbon disulfide. **13.2** 0.638  $m$ . **13.3** 8.92  $m$ .  
**13.4** 13.8  $m$ . **13.5**  $2.9 \times 10^{-4}\text{ M}$ . **13.6** 37.8 mmHg;

- 4.4 mmHg. **13.7**  $101.3^\circ C$ ;  $-4.48^\circ C$ . **13.8** 0.066  $m$ ;  $1.3 \times 10^2\text{ g/mol}$ . **13.9**  $2.60 \times 10^4\text{ g/mol}$ . **13.10** 1.21.

# 14



A hot platinum wire glows when held over a concentrated ammonia solution. The oxidation of ammonia to produce nitric oxide, catalyzed by platinum, is highly exothermic.

## Chemical Kinetics

### CHAPTER OUTLINE

- 14.1** The Rate of a Reaction 455
- 14.2** The Rate Laws 459
  - Experimental Determination of Rate Laws
- 14.3** Relation Between Reactant Concentrations and Time 463
  - First-Order Reactions • Second-Order Reactions • Zero-Order Reactions
- 14.4** Activation Energy and Temperature Dependence of Rate Constants 471
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- 14.5** Reaction Mechanisms 477
  - Rate Laws and Elementary Steps
- 14.6** Catalysis 480
  - Heterogeneous Catalysis • Homogeneous Catalysis • Enzyme Catalysis



### Activity Summary

1. Interactivity: Rate Laws (14.2)
2. Animation: Activation Energy (14.4)
3. Animation: Orientation of Collision (14.4)
4. Interactivity: Mechanisms and Rates (14.5)
5. Animation: Catalysis (14.6)

### ESSENTIAL CONCEPTS

**Rate of a Reaction** The rate of a reaction measures how fast a reactant is consumed or how fast a product is formed. The rate is expressed as a ratio of the change in concentration to elapsed time.

**Rate Laws** Experimental measurement of the rate leads to the rate law for the reaction, which expresses the rate in terms of the rate constant and the concentrations of the reactants. The dependence of rate on concentrations gives the order of a reaction. A reaction can be described as zero order if the rate does not depend on the concentration of the reactant, or first order if it depends on the reactant raised to the first power. Higher orders and fractional orders are also known. An important characteristic of reaction rates is the time required for the concentration of a reactant to decrease to half of its initial concentration, called the half-life. For first-order reactions, the half-life is independent of the initial concentration.

**Temperature Dependence of Rate Constants** To react, molecules must possess energy equal to or greater than the activation energy. The rate constant generally increases with increasing temperature. The Arrhenius equation relates the rate constant to activation energy and temperature.

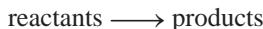
**Reaction Mechanism** The progress of a reaction can be broken into a series of elementary steps at the molecular level, and the sequence of such steps is the mechanism of the reaction. Elementary steps can be unimolecular, involving one molecule, bimolecular, where two molecules react, or in rare cases, termolecular, involving the simultaneous encounter of three molecules. The rate of a reaction having more than one elementary step is governed by the slowest step, called the rate-determining step.

**Catalysis** A catalyst speeds up the rate of a reaction without itself being consumed. In heterogeneous catalysis, the reactants and catalyst are in different phases. In homogeneous catalysis, the reactants and catalyst are dispersed in a single phase. Enzymes, which are highly efficient catalysts, play a central role in all living systems.

## 14.1 The Rate of a Reaction

The area of chemistry concerned with the speed, or rate, at which a chemical reaction occurs is called **chemical kinetics**. The word “kinetic” suggests movement or change; in Chapter 5 we defined kinetic energy as the energy available because of the motion of an object. Here kinetics refers to the rate of a reaction, or the **reaction rate**, which is *the change in concentration of a reactant or a product with time (M/s)*.

We know that any reaction can be represented by the general equation



This equation tells us that, during the course of a reaction, reactant molecules are consumed while product molecules are formed. As a result, we can follow the progress of a reaction by monitoring either the decrease in concentration of the reactants or the increase in concentration of the products.

Figure 14.1 shows the progress of a simple reaction in which A molecules are converted to B molecules (for example, the conversion of *cis*-1,2-dichloroethylene to *trans*-1,2-dichloroethylene shown on p. 365):



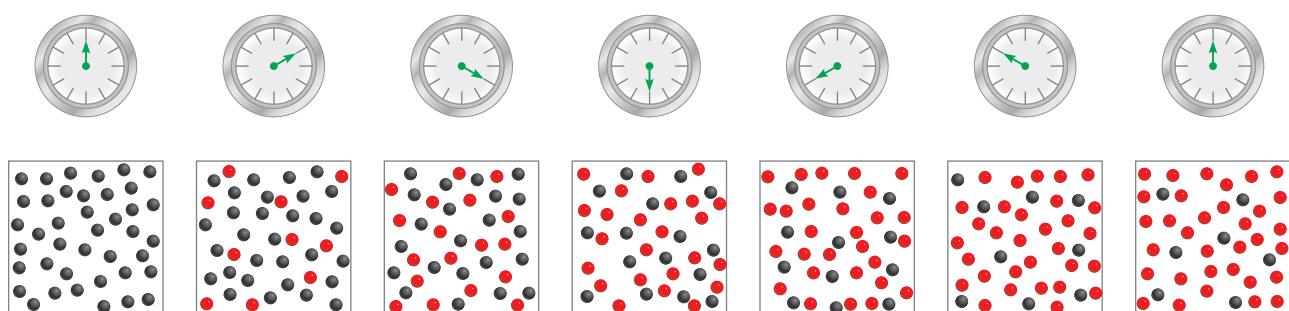
The decrease in the number of A molecules and the increase in the number of B molecules with time are shown in Figure 14.2. In general, it is more convenient to express the rate in terms of change in concentration with time. Thus, for the preceding reaction we can express the rate as

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} \quad \text{or} \quad \text{rate} = \frac{\Delta[\text{B}]}{\Delta t}$$

Recall that  $\Delta$  denotes the difference between the final and initial state.

in which  $\Delta[\text{A}]$  and  $\Delta[\text{B}]$  are the changes in concentration (in molarity) over a period  $\Delta t$ . Because the concentration of A *decreases* during the time interval,  $\Delta[\text{A}]$  is a negative quantity. The rate of a reaction is a positive quantity, so a minus sign is needed in the rate expression to make the rate positive. On the other hand, the rate of product formation does not require a minus sign because  $\Delta[\text{B}]$  is a positive quantity (the concentration of B *increases* with time).

For more complex reactions, we must be careful in writing the rate expression. Consider, for example, the reaction

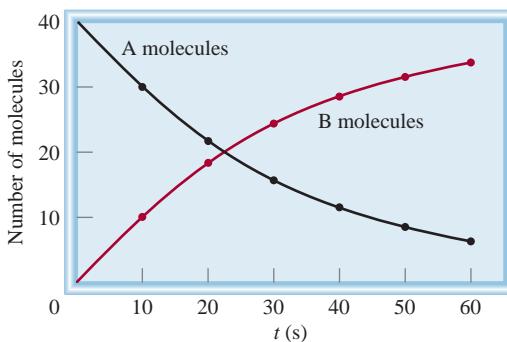


**Figure 14.1**

The progress of reaction  $\text{A} \longrightarrow \text{B}$  at 10-s intervals over a period of 60 s. Initially, only A molecules (gray spheres) are present. As time progresses, B molecules (red spheres) are formed.

**Figure 14.2**

The rate of reaction  $A \longrightarrow B$ , represented as the decrease of A molecules with time and as the increase of B molecules with time.



Two moles of A disappear for each mole of B that forms—that is, the rate at which B forms is one half the rate at which A disappears. We write the rate as either

$$\text{rate} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} \quad \text{or} \quad \text{rate} = \frac{\Delta[B]}{\Delta t}$$

For the reaction



the rate is given by

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

**Example 14.1**

Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products:

- (a)  $I^-(aq) + OCl^-(aq) \longrightarrow Cl^-(aq) + OI^-(aq)$
- (b)  $3O_2(g) \longrightarrow 2O_3(g)$
- (c)  $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

**Solution** (a) Because each of the stoichiometric coefficients equals 1,

$$\text{rate} = -\frac{\Delta[I^-]}{\Delta t} = -\frac{\Delta[OCl^-]}{\Delta t} = \frac{\Delta[Cl^-]}{\Delta t} = \frac{\Delta[OI^-]}{\Delta t}$$

(b) Here the coefficients are 3 and 2, so

$$\text{rate} = -\frac{1}{3} \frac{\Delta[O_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[O_3]}{\Delta t}$$

(c) In this reaction

$$\text{rate} = -\frac{1}{4} \frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5} \frac{\Delta[O_2]}{\Delta t} = \frac{1}{4} \frac{\Delta[NO]}{\Delta t} = \frac{1}{6} \frac{\Delta[H_2O]}{\Delta t}$$

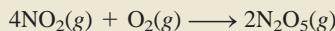
**Similar problem: 14.5.**

**Practice Exercise** Write the rate expression for the following reaction:



## Example 14.2

Consider the reaction



Suppose that, at a particular moment during the reaction, molecular oxygen is reacting at the rate of  $0.024 \text{ M/s}$ . (a) At what rate is  $\text{N}_2\text{O}_5$  being formed? (b) At what rate is  $\text{NO}_2$  reacting?

**Strategy** To calculate the rate of formation of  $\text{N}_2\text{O}_5$  and disappearance of  $\text{NO}_2$ , we need to express the rate of the reaction in terms of the stoichiometric coefficients as in Example 14.1:

$$\text{rate} = -\frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

We are given

$$\frac{\Delta[\text{O}_2]}{\Delta t} = -0.024 \text{ M/s}$$

where the minus sign shows that the concentration of  $\text{O}_2$  is decreasing with time.

**Solution** (a) From the preceding rate expression, we have

$$-\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

Therefore,

$$\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = -2(-0.024 \text{ M/s}) = 0.048 \text{ M/s}$$

(b) Here we have

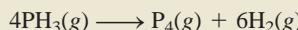
$$-\frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t}$$

so

$$\frac{\Delta[\text{NO}_2]}{\Delta t} = 4(-0.024 \text{ M/s}) = -0.096 \text{ M/s}$$

**Similar problem: 14.6.**

**Practice Exercise** Consider the reaction



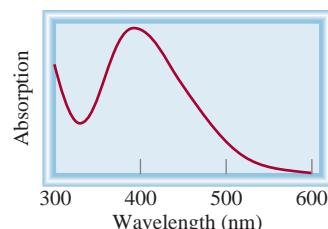
Suppose that, at a particular moment during the reaction, molecular hydrogen is being formed at the rate of  $0.078 \text{ M/s}$ . (a) At what rate is  $\text{P}_4$  being formed? (b) At what rate is  $\text{PH}_3$  reacting?

Depending on the nature of the reaction, there are a number of ways in which to measure reaction rate. For example, in aqueous solution, molecular bromine reacts with formic acid ( $\text{HCOOH}$ ) as



**Figure 14.3**

The decrease in bromine concentration as time elapses shows up as a loss of color (from left to right).

**Figure 14.4**

Plot of absorption of bromine versus wavelength. The maximum absorption of visible light by bromine occurs at 393 nm. As the reaction progresses, the absorption, which is proportional to  $[Br_2]$ , decreases with time, indicating a depletion in bromine.

Molecular bromine is reddish brown. All other species in the reaction are colorless. As the reaction progresses, the concentration of  $Br_2$  steadily decreases and its color fades (Figure 14.3). Thus, the change in concentration (which is evident by the intensity of the color) with time can be followed with a spectrometer (Figure 14.4). We can determine the reaction rate graphically by plotting the concentration of bromine versus time, as Figure 14.5 shows. The rate of the reaction at a particular instant is given by the slope of the tangent (which is  $\Delta[Br_2]/\Delta t$ ) at that instant. In a certain experiment, we find that the rate is  $2.96 \times 10^{-5} M/s$  at 100 s after the start of the reaction,  $2.09 \times 10^{-5} M/s$  at 200 s, and so on. Because generally the rate is proportional to the concentration of the reactant, it is not surprising that its value falls as the concentration of bromine decreases.

If one of the products or reactants of a reaction is a gas, we can use a manometer to find the reaction rate. To illustrate this method, let us consider the decomposition of hydrogen peroxide:



In this case, the rate of decomposition can be conveniently determined by measuring the rate of oxygen evolution with a manometer (Figure 14.6). The oxygen pressure can be readily converted to concentration by using the ideal gas equation [Equation (5.8)]:

$$PV = nRT$$

or

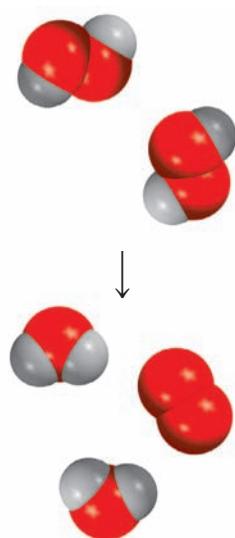
$$P = \frac{n}{V} RT = MRT$$

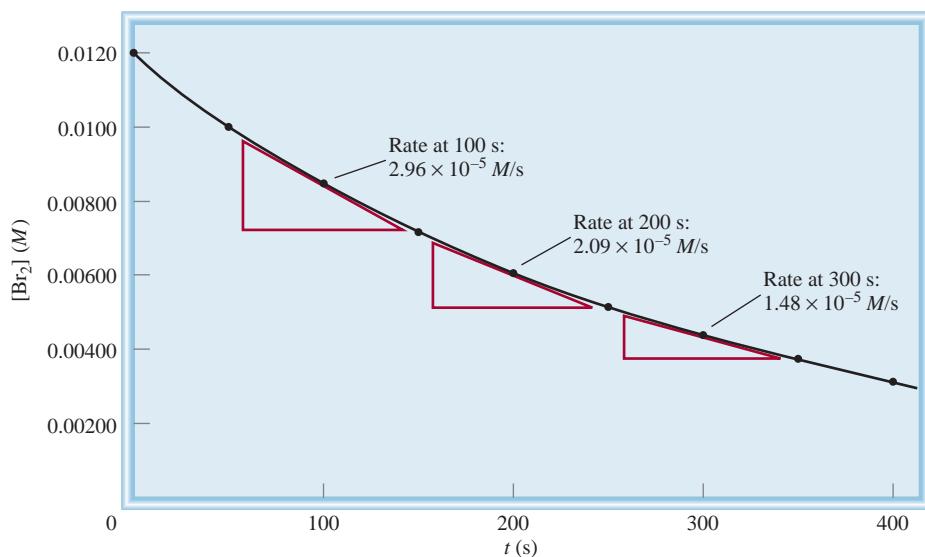
in which  $n/V$  gives the molarity ( $M$ ) of oxygen gas. Rearranging the equation, we get

$$M = \frac{1}{RT} P$$

The reaction rate, which is given by the rate of oxygen production, can now be written as

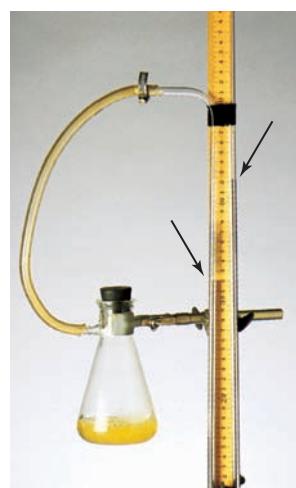
$$\text{rate} = \frac{\Delta [O_2]}{\Delta t} = \frac{1}{RT} \frac{\Delta P}{\Delta t}$$



**Figure 14.5**

The instantaneous rates of the reaction between molecular bromine and formic acid at  $t = 100$  s,  $200$  s, and  $300$  s are given by the slopes of the tangents at these times.

If a reaction either consumes or generates ions, its rate can be measured by monitoring electrical conductance. If  $H^+$  ion is the reactant or product, we can determine the reaction rate by measuring the solution's pH as a function of time.

**Figure 14.6**

The rate of hydrogen peroxide decomposition can be measured with a manometer, which shows the increase in the oxygen gas pressure with time. The arrows show the mercury levels in the U tube.

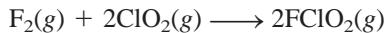
## 14.2 The Rate Laws

One way to study the effect of reactant concentration on reaction rate is to determine how the initial rate depends on the starting concentrations. In general, it is preferable to measure the initial rate because as the reaction proceeds, the concentrations of the reactants decrease and it may become difficult to measure the changes accurately. Also, there may be a reverse reaction such that



which would introduce error in the rate measurement. Both of these complications are virtually absent during the early stages of the reaction.

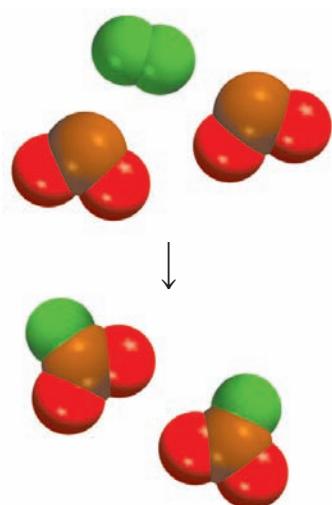
Table 14.1 shows three experimental rate measurements for the reaction



Looking at table entries 1 and 3, we see that if we double  $[F_2]$  while holding  $[\text{ClO}_2]$  constant, the rate doubles. Thus, the rate is directly proportional to  $[F_2]$ . Similarly, the

**TABLE 14.1** Rate Data for the Reaction Between  $F_2$  and  $\text{ClO}_2$ 

| $[F_2]$ (M) | $[\text{ClO}_2]$ (M) | Initial Rate (M/s)   |
|-------------|----------------------|----------------------|
| 1. 0.10     | 0.010                | $1.2 \times 10^{-3}$ |
| 2. 0.10     | 0.040                | $4.8 \times 10^{-3}$ |
| 3. 0.20     | 0.010                | $2.4 \times 10^{-3}$ |



data in entries 1 and 2 show that when we quadruple  $[ClO_2]$  at constant  $[F_2]$ , the rate increases by four times, so that the rate is also directly proportional to  $[ClO_2]$ . We can summarize these observations by writing

$$\begin{aligned} \text{rate} &\propto [F_2][ClO_2] \\ \text{rate} &= k[F_2][ClO_2] \end{aligned}$$



The term  $k$  is the **rate constant**, a constant of proportionality between the reaction rate and the concentrations of the reactants. This equation is known as the **rate law**, an expression relating the rate of a reaction to the rate constant and the concentrations of the reactants. From the reactant concentrations and the initial rate, we can also calculate the rate constant. Using the first entry of data in Table 14.1, we can write

$$\begin{aligned} k &= \frac{\text{rate}}{[F_2][ClO_2]} \\ &= \frac{1.2 \times 10^{-3} M/s}{(0.10 M)(0.010 M)} \\ &= 1.2/M \cdot s \end{aligned}$$

For a general reaction of the type



the rate law takes the form

$$\text{rate} = k[A]^x[B]^y \quad (14.1)$$

Note that  $x$  and  $y$  are **not** related to  $a$  and  $b$ . They must be determined experimentally.

If we know the values of  $k$ ,  $x$ , and  $y$ , as well as the concentrations of A and B, we can use the rate law to calculate the rate of the reaction. Like  $k$ ,  $x$  and  $y$  must be determined experimentally. *The sum of the powers to which all reactant concentrations appearing in the rate law are raised* is called the overall **reaction order**. In the rate law expression shown, the overall reaction order is given by  $x + y$ . For the reaction involving  $F_2$  and  $ClO_2$ , the overall order is  $1 + 1$ , or 2. We say that the reaction is first order in  $F_2$  and first order in  $ClO_2$ , or second order overall. Note that reaction order is *always* determined by reactant concentrations and never by product concentrations.

Reaction order enables us to appreciate better the dependence of rate on reactant concentrations. Suppose, for example, that, for a certain reaction,  $x = 1$  and  $y = 2$ . The rate law for the reaction from Equation (14.1) is

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

This reaction is first order in A, second order in B, and third order overall ( $1 + 2 = 3$ ). Let us assume that initially  $[A] = 1.0 M$  and  $[B] = 1.0 M$ . The rate law tells us that if we double the concentration of A from  $1.0 M$  to  $2.0 M$  at constant  $[B]$ , we also double the reaction rate:

$$\begin{aligned} \text{for } [A] &= 1.0 M & \text{rate}_1 &= k(1.0 M)(1.0 M)^2 \\ & & &= k(1.0 M^3) \\ \text{for } [A] &= 2.0 M & \text{rate}_2 &= k(2.0 M)(1.0 M)^2 \\ & & &= k(2.0 M^3) \end{aligned}$$

Hence,

$$\text{rate}_2 = 2(\text{rate}_1)$$

On the other hand, if we double the concentration of B from  $1.0\text{ M}$  to  $2.0\text{ M}$  at constant [A], the reaction rate will increase by a factor of 4 because of the power 2 in the exponent:

$$\begin{aligned} \text{for } [\text{B}] = 1.0\text{ M} \quad \text{rate}_1 &= k(1.0\text{ M})(1.0\text{ M})^2 \\ &= k(1.0\text{ M}^3) \\ \text{for } [\text{B}] = 2.0\text{ M} \quad \text{rate}_2 &= k(1.0\text{ M})(2.0\text{ M})^2 \\ &= k(4.0\text{ M}^3) \end{aligned}$$

Hence,

$$\text{rate}_2 = 4(\text{rate}_1)$$

If, for a certain reaction,  $x = 0$  and  $y = 1$ , then the rate law is

$$\begin{aligned} \text{rate} &= k[\text{A}]^0[\text{B}] \\ &= k[\text{B}] \end{aligned}$$

This reaction is zero order in A, first order in B, and first order overall. Thus, the rate of this reaction is *independent* of the concentration of A.

## Experimental Determination of Rate Laws

If a reaction involves only one reactant, the rate law can be readily determined by measuring the initial rate of the reaction as a function of the reactant's concentration. For example, if the rate doubles when the concentration of the reactant doubles, then the reaction is first order in the reactant. If the rate quadruples when the concentration doubles, the reaction is second order in the reactant.

For a reaction involving more than one reactant, we can find the rate law by measuring the dependence of the reaction rate on the concentration of each reactant, one at a time. We fix the concentrations of all but one reactant and record the rate of the reaction as a function of the concentration of that reactant. Any changes in the rate must be due only to changes in that substance. The dependence thus observed gives us the order in that particular reactant. The same procedure is then applied to the next reactant, and so on. This approach is known as the *isolation method*.

### Example 14.3

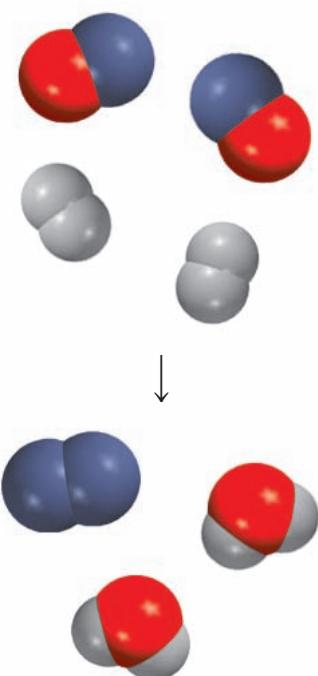
The reaction of nitric oxide with hydrogen at  $1280^\circ\text{C}$  is



From the following data collected at this temperature, determine (a) the rate law, (b) the rate constant, and (c) the rate of the reaction when  $[\text{NO}] = 12.0 \times 10^{-3}\text{ M}$  and  $[\text{H}_2] = 6.0 \times 10^{-3}\text{ M}$ .

| Experiment | $[\text{NO}]\text{ (M)}$ | $[\text{H}_2]\text{ (M)}$ | Initial Rate ( $\text{M/s}$ ) |
|------------|--------------------------|---------------------------|-------------------------------|
| 1          | $5.0 \times 10^{-3}$     | $2.0 \times 10^{-3}$      | $1.3 \times 10^{-5}$          |
| 2          | $10.0 \times 10^{-3}$    | $2.0 \times 10^{-3}$      | $5.0 \times 10^{-5}$          |
| 3          | $10.0 \times 10^{-3}$    | $4.0 \times 10^{-3}$      | $10.0 \times 10^{-5}$         |

(Continued)



**Strategy** We are given a set of concentration and reaction rate data and asked to determine the rate law and the rate constant. We assume that the rate law takes the form

$$\text{rate} = k[\text{NO}]^x[\text{H}_2]^y$$

How do we use the data to determine  $x$  and  $y$ ? Once the orders of the reactants are known, we can calculate  $k$  from any set of rate and concentrations. Finally, the rate law enables us to calculate the rate at any concentrations of NO and H<sub>2</sub>.

**Solution** (a) Experiments 1 and 2 show that when we double the concentration of NO at constant concentration of H<sub>2</sub>, the rate quadruples. Taking the ratio of the rates from these two experiments

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{5.0 \times 10^{-5} \text{ M/s}}{1.3 \times 10^{-5} \text{ M/s}} \approx 4 = \frac{k(10.0 \times 10^{-3} \text{ M})^x(2.0 \times 10^{-3} \text{ M})^y}{k(5.0 \times 10^{-3} \text{ M})^x(2.0 \times 10^{-3} \text{ M})^y}$$

Therefore,

$$\frac{(10.0 \times 10^{-3} \text{ M})^x}{(5.0 \times 10^{-3} \text{ M})^x} = 2^x = 4$$

or  $x = 2$ , that is, the reaction is second order in NO. Experiments 2 and 3 indicate that doubling [H<sub>2</sub>] at constant [NO] doubles the rate. Here we write the ratio as

$$\frac{\text{rate}_3}{\text{rate}_2} = \frac{10.0 \times 10^{-5} \text{ M/s}}{5.0 \times 10^{-5} \text{ M/s}} = 2 = \frac{k(10.0 \times 10^{-3} \text{ M})^x(4.0 \times 10^{-3} \text{ M})^y}{k(10.0 \times 10^{-3} \text{ M})^x(2.0 \times 10^{-3} \text{ M})^y}$$

Therefore,

$$\frac{(4.0 \times 10^{-3} \text{ M})^y}{(2.0 \times 10^{-3} \text{ M})^y} = 2^y = 2$$

or  $y = 1$ , that is, the reaction is first order in H<sub>2</sub>. Hence, the rate law is given by

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

which shows that it is a (2 + 1) or third-order reaction overall.

(b) The rate constant  $k$  can be calculated using the data from any one of the experiments. Rearranging the rate law, we get

$$k = \frac{\text{rate}}{[\text{NO}]^2[\text{H}_2]}$$

The data from experiment 2 give us

$$\begin{aligned} k &= \frac{5.0 \times 10^{-5} \text{ M/s}}{(10.0 \times 10^{-3} \text{ M})^2(2.0 \times 10^{-3} \text{ M})} \\ &= 2.5 \times 10^2 \text{ M}^{-2} \cdot \text{s}^{-1} \end{aligned}$$

(c) Using the known rate constant and concentrations of NO and H<sub>2</sub>, we write

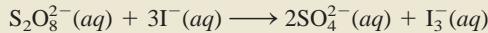
$$\begin{aligned} \text{rate} &= (2.5 \times 10^2 \text{ M}^{-2} \cdot \text{s})(12.0 \times 10^{-3} \text{ M})^2(6.0 \times 10^{-3} \text{ M}) \\ &= 2.2 \times 10^{-4} \text{ M/s} \end{aligned}$$

(Continued)

**Comment** Note that the reaction is first order in H<sub>2</sub>, whereas the stoichiometric coefficient for H<sub>2</sub> in the balanced equation is 2. The order of a reactant is not related to the stoichiometric coefficient of the reactant in the overall balanced equation.

**Similar problem:** 14.17.

**Practice Exercise** The reaction of peroxydisulfate ion (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) with iodide ion (I<sup>-</sup>) is



From the following data collected at a certain temperature, determine the rate law and calculate the rate constant.

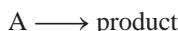
| Experiment | [S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ] (M) | [I <sup>-</sup> ] (M) | Initial Rate (M/s)     |
|------------|--|-----------------------|------------------------|
| 1          | 0.080  | 0.034                 | 2.2 × 10 <sup>-4</sup> |
| 2          | 0.080  | 0.017                 | 1.1 × 10 <sup>-4</sup> |
| 3          | 0.16   | 0.017                 | 2.2 × 10 <sup>-4</sup> |

## 14.3 Relation Between Reactant Concentrations and Time

Rate laws enable us to calculate the rate of a reaction from the rate constant and reactant concentrations. They can also be converted into equations that enable us to determine the concentrations of reactants at any time during the course of a reaction. We will illustrate this application by considering first one of the simplest kind of rate laws—that applying to reactions that are first order overall.

### First-Order Reactions

A **first-order reaction** is a reaction whose rate depends on the reactant concentration raised to the first power. In a first-order reaction of the type



the rate is

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t}$$

From the rate law, we also know that

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

**For a first-order reaction, doubling the concentration of the reactant doubles the rate.**

Thus,

$$-\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}] \quad (14.2)$$

We can determine the units of the first-order rate constant *k* by transposing:

$$k = -\frac{\Delta[\text{A}]}{[\text{A}]} \frac{1}{\Delta t}$$

Because the unit for  $\Delta[A]$  and  $[A]$  is  $M$  and that for  $\Delta t$  is  $s$ , the unit for  $k$  is

$$\frac{M}{M \text{ s}} = \frac{1}{\text{s}} = \text{s}^{-1}$$

In differential form, Equation (14.2) becomes

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

Rearranging, we get

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

Integrating between  $t = 0$  and  $t = t$  gives

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_0^t dt$$

$$\ln[A]_t - \ln[A]_0 = -kt$$

or  $\ln \frac{[A]_t}{[A]_0} = -kt$

(The minus sign does not enter into the evaluation of units.) Using calculus, we can show from Equation (14.2) that

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad (14.3)$$

in which  $\ln$  is the natural logarithm, and  $[A]_0$  and  $[A]_t$  are the concentrations of A at times  $t = 0$  and  $t = t$ , respectively. It should be understood that  $t = 0$  need not correspond to the beginning of the experiment; it can be any time when we choose to monitor the change in the concentration of A.

Equation (14.3) can be rearranged as follows:

$$\ln [A]_t - \ln [A]_0 = -kt$$

or

$$\ln [A]_t = -kt + \ln [A]_0 \quad (14.4)$$

Equation (14.4) has the form of the linear equation  $y = mx + b$ , in which  $m$  is the slope of the line that is the graph of the equation:

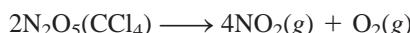
$$\begin{array}{c} \ln [A]_t = (-k)(t) + \ln [A]_0 \\ \uparrow \qquad \uparrow \qquad \uparrow \qquad \uparrow \\ y \quad = \quad m \quad x \quad + \quad b \end{array}$$

Thus, a plot of  $\ln [A]_t$  versus  $t$  (or  $y$  versus  $x$ ) gives a straight line with a slope of  $-k$  (or  $m$ ). This enables us to calculate the rate constant  $k$ . Figure 14.7 shows the characteristics of a first-order reaction.

There are many known first-order reactions. All nuclear decay processes are first order (see Chapter 21). Another example is the decomposition of ethane ( $C_2H_6$ ) into highly reactive methyl radicals ( $CH_3$ ):

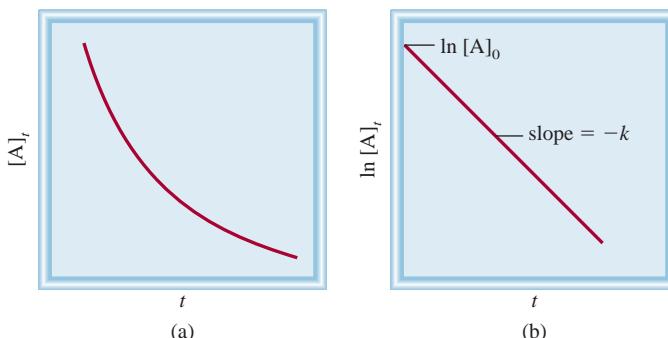


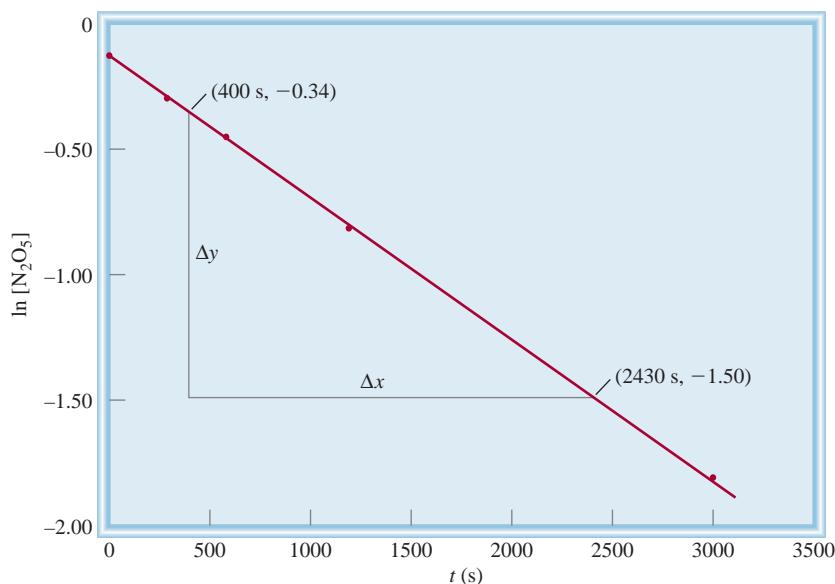
Now let us determine graphically the order and rate constant of the decomposition of nitrogen pentoxide in carbon tetrachloride ( $CCl_4$ ) solvent at  $45^\circ C$ :



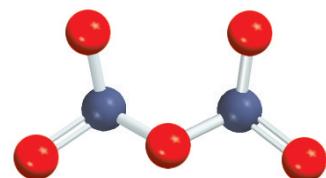
**Figure 14.7**

First-order reaction characteristics: (a) Decrease of reactant concentration with time; (b) plot of the straight-line relationship to obtain the rate constant. The slope of the line is equal to  $-k$ .





**Figure 14.8**  
Plot of  $\ln [N_2O_5]$  versus time. The rate constant can be determined from the slope of the straight line.



This table shows the variation of  $N_2O_5$  concentration with time, and the corresponding  $\ln [N_2O_5]$  values

| $t(s)$ | $[N_2O_5]$ | $\ln [N_2O_5]$ |
|--------|------------|----------------|
| 0      | 0.91       | -0.094         |
| 300    | 0.75       | -0.29          |
| 600    | 0.64       | -0.45          |
| 1200   | 0.44       | -0.82          |
| 3000   | 0.16       | -1.83          |

Applying Equation (14.4) we plot  $\ln [N_2O_5]$  versus  $t$ , as shown in Figure 14.8. The fact that the points lie on a straight line shows that the rate law is first order. Next, we determine the rate constant from the slope. We select two points far apart on the line and subtract their  $y$  and  $x$  values as

$$\begin{aligned} \text{slope } (m) &= \frac{\Delta y}{\Delta x} \\ &= \frac{-1.50 - (-0.34)}{(2430 - 400) \text{ s}} \\ &= -5.7 \times 10^{-4} \text{ s}^{-1} \end{aligned}$$

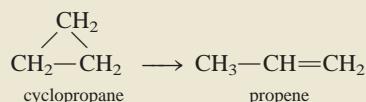
Because  $m = -k$ , we get  $k = 5.7 \times 10^{-4} \text{ s}^{-1}$ .



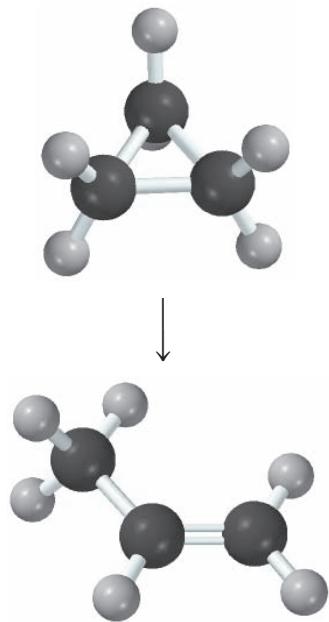
$N_2O_5$  decomposes to give  $NO_2$  (brown color) and colorless  $O_2$  gases.

### Example 14.4

The conversion of cyclopropane to propene in the gas phase is a first-order reaction with a rate constant of  $6.7 \times 10^{-4} \text{ s}^{-1}$  at  $500^\circ\text{C}$ .



(Continued)



- (a) If the initial concentration of cyclopropane was  $0.25\text{ M}$ , what is the concentration after 8.8 min? (b) How long (in minutes) will it take for the concentration of cyclopropane to decrease from  $0.25\text{ M}$  to  $0.15\text{ M}$ ? (c) How long (in minutes) will it take to convert 74 percent of the starting material?

**Strategy** The relationship between the concentrations of a reactant at different times in a first-order reaction is given by Equation (14.3) or (14.4). In (a) we are given  $[A]_0 = 0.25\text{ M}$  and asked for  $[A]_t$  after 8.8 min. In (b) we are asked to calculate the time it takes for cyclopropane to decrease in concentration from  $0.25\text{ M}$  to  $0.15\text{ M}$ . No concentration values are given for (c). However, if initially we have 100 percent of the compound and 74 percent has reacted, then what is left must be  $(100\% - 74\%)$ , or 26 percent. Thus, the ratio of the percentages will be equal to the ratio of the actual concentrations; that is,  $[A]_t/[A]_0 = 26\%/100\%$ , or  $0.26/1.00$ .

**Solution** (a) In applying Equation (14.4), we note that because  $k$  is given in units of  $\text{s}^{-1}$ , we must first convert 8.8 min to seconds:

$$8.8 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} = 528 \text{ s}$$

We write

$$\begin{aligned}\ln [A]_t &= -kt + \ln [A]_0 \\ &= -(6.7 \times 10^{-4} \text{ s}^{-1})(528 \text{ s}) + \ln(0.25) \\ &= -1.74\end{aligned}$$

Hence,

$$[A]_t = e^{-1.74} = 0.18\text{ M}$$

Note that in the  $\ln [A]_0$  term,  $[A]_0$  is expressed as a dimensionless quantity (0.25) because we cannot take the logarithm of units.

(b) Using Equation (14.3),

$$\begin{aligned}\ln \frac{0.15\text{ M}}{0.25\text{ M}} &= -(6.7 \times 10^{-4} \text{ s}^{-1})t \\ t &= 7.6 \times 10^2 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \\ &= 13 \text{ min}\end{aligned}$$

(c) From Equation (14.3),

$$\begin{aligned}\ln \frac{0.26}{1.00} &= -(6.7 \times 10^{-4} \text{ s}^{-1})t \\ t &= 2.0 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 33 \text{ min}\end{aligned}$$

**Similar problems:** 14.24(b), 14.25(a).

**Practice Exercise** The reaction  $2\text{A} \longrightarrow \text{B}$  is first order in A with a rate constant of  $2.8 \times 10^{-2} \text{ s}^{-1}$  at  $80^\circ\text{C}$ . How long (in seconds) will it take for A to decrease from  $0.88\text{ M}$  to  $0.14\text{ M}$ ?

### Half-Life

The **half-life** of a reaction,  $t_{\frac{1}{2}}$ , is the time required for the concentration of a reactant to decrease to half of its initial concentration. We can obtain an expression for  $t_{\frac{1}{2}}$  for a first-order reaction as shown next. Rearranging Equation (14.3) we get

$$t = \frac{1}{k} \ln \frac{[A]_0}{[A]_t}$$

By the definition of half-life, when  $t = t_{\frac{1}{2}}$ ,  $[A]_t = [A]_0/2$ , so

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

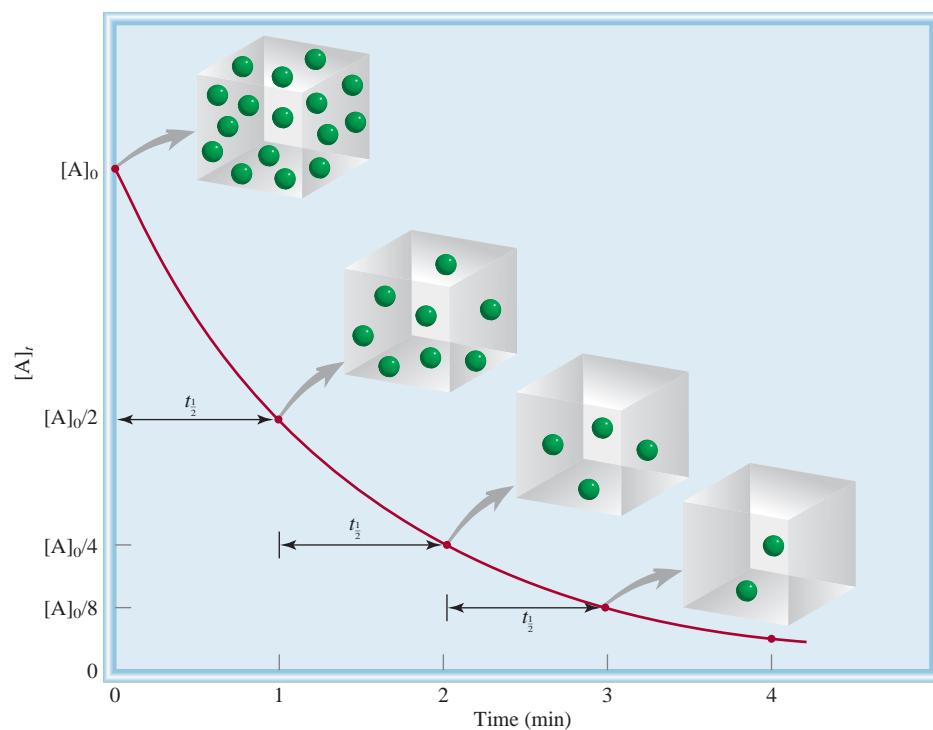
or

$$t_{\frac{1}{2}} = \frac{1}{k} \ln 2 = \frac{0.693}{k} \quad (14.5)$$

Equation (14.5) tells us that the half-life of a first-order reaction is *independent* of the initial concentration of the reactant. Thus, it takes the same time for the concentration of the reactant to decrease from  $1.0\text{ M}$  to  $0.50\text{ M}$ , say, as it does for a decrease in concentration from  $0.10\text{ M}$  to  $0.050\text{ M}$  (Figure 14.9). Measuring the half-life of a reaction is one way to determine the rate constant of a first-order reaction.

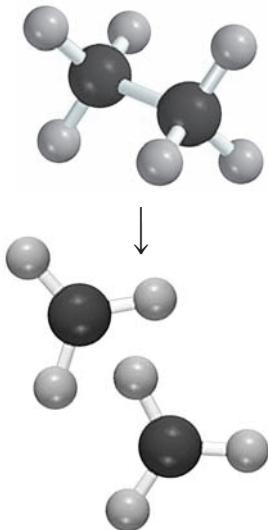
This analogy is helpful in understanding Equation (14.5). The duration of a college undergraduate's career, assuming the student does not take any time off, is 4 years. Thus, the half-life of his or her stay at the college is 2 years. This half-life is not affected by how many other students are present. Similarly, the half-life of a first-order reaction is concentration independent.

The usefulness of  $t_{\frac{1}{2}}$  is that it gives us an estimate of the magnitude of the rate constant—the shorter the half-life, the larger the  $k$ . Consider, for example, two radioactive isotopes that are used in nuclear medicine:  $^{24}\text{Na}$  ( $t_{\frac{1}{2}} = 14.7\text{ h}$ ) and  $^{60}\text{Co}$  ( $t_{\frac{1}{2}} = 5.3\text{ yr}$ ). It is obvious that the  $^{24}\text{Na}$  isotope decays faster because it has a shorter half-life. If we started with 1 mole of each of the isotopes, most of the  $^{24}\text{Na}$  would be gone in a week, whereas the  $^{60}\text{Co}$  sample would be mostly intact.



**Figure 14.9**

A plot of  $[A]$  versus time for the first-order reaction  $\text{A} \longrightarrow \text{products}$ . The half-life of the reaction is 1 min. After the elapse of each half-life, the concentration of  $\text{A}$  is halved.



**Similar problem:** 14.24(a).

### Example 14.5

The decomposition of ethane ( $\text{C}_2\text{H}_6$ ) to methyl radicals is a first-order reaction with a rate constant of  $5.36 \times 10^{-4} \text{ s}^{-1}$  at  $700^\circ\text{C}$ :



Calculate the half-life of the reaction in minutes.

**Strategy** To calculate the half-life of a first-order reaction, we use Equation (14.5). A conversion is needed to express the half-life in minutes.

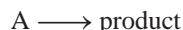
**Solution** For a first-order reaction, we only need the rate constant to calculate the half-life of the reaction. From Equation (14.5)

$$\begin{aligned} t_{\frac{1}{2}} &= \frac{0.693}{k} \\ &= \frac{0.693}{5.36 \times 10^{-4} \text{ s}^{-1}} \\ &= 1.29 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \\ &= 21.5 \text{ min} \end{aligned}$$

**Practice Exercise** Calculate the half-life of the decomposition of  $\text{N}_2\text{O}_5$ , discussed on p. 465.

## Second-Order Reactions

A **second-order reaction** is a reaction whose rate depends on the concentration of one reactant raised to the second power or on the concentrations of two different reactants, each raised to the first power. The simpler type involves only one kind of reactant molecule:



for which

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t}$$

From the rate law,

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

As before, we can determine the units of  $k$  by writing

$$k = \frac{\text{rate}}{[\text{A}]^2} = \frac{\text{M/s}}{\text{M}^2} = 1/\text{M} \cdot \text{s}$$

Another type of second-order reaction is



and the rate law is given by

$$\text{rate} = k[\text{A}][\text{B}]$$

The reaction is first order in A and first order in B, so it has an overall reaction order of 2.

Using calculus, we can obtain the following expressions for “A → product” second-order reactions:

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt \quad (14.6)$$

Equation (14.6) has the form of a linear equation. As Figure 14.10 shows, a plot of  $1/[A]_t$  versus  $t$  gives a straight line with slope =  $k$  and  $y$  intercept =  $1/[A]_0$ . (The corresponding equation for “A + B → product” reactions is too complex for our discussion.)

We can obtain an equation for the half-life of a second-order reaction by setting  $[A]_t = [A]_0/2$  in Equation (14.6):

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

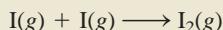
Solving for  $t_{\frac{1}{2}}$  we obtain

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0} \quad (14.7)$$

Note that the half-life of a second-order reaction is inversely proportional to the initial reactant concentration. This result makes sense because the half-life should be shorter in the early stage of the reaction when more reactant molecules are present to collide with each other. Measuring the half-lives at different initial concentrations is one way to distinguish between a first-order and a second-order reaction.

### Example 14.6

Iodine atoms combine to form molecular iodine in the gas phase



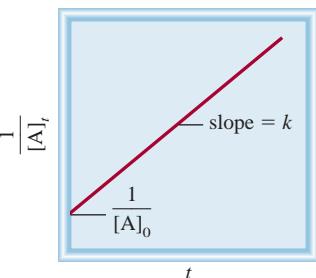
This reaction follows second-order kinetics and has the high rate constant  $7.0 \times 10^9/M \cdot s$  at  $23^\circ C$ . (a) If the initial concentration of I was  $0.086 M$ , calculate the concentration after 2.0 min. (b) Calculate the half-life of the reaction if the initial concentration of I is  $0.60 M$  and if it is  $0.42 M$ .

**Strategy** (a) The relationship between the concentrations of a reactant at different times is given by the integrated rate law. Because this is a second-order reaction, we use Equation (14.6). (b) We are asked to calculate the half-life. The half-life for a second-order reaction is given by Equation (14.7).

**Solution** (a) To calculate the concentration of a species at a later time of a second-order reaction, we need the initial concentration and the rate constant. Applying Equation (14.6),

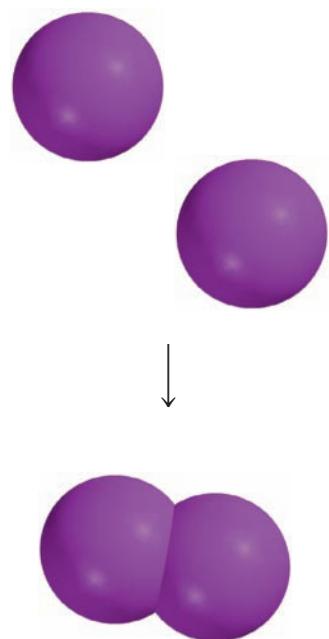
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$\frac{1}{[A]_t} = (7.0 \times 10^9/M \cdot s) \left( 2.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \right) + \frac{1}{0.086 M}$$



**Figure 14.10**

A plot of  $1/[A]_t$  versus  $t$  for a second-order reaction. The slope of the line is equal to  $k$ .



(Continued)

where  $[A]_t$  is the concentration at  $t = 2.0$  min. Solving the equation, we get

$$[A]_t = 1.2 \times 10^{-12} M$$

This is such a low concentration that it is virtually undetectable. The very large rate constant for the reaction means that practically all the I atoms combine after only 2.0 min of reaction time.

- (b) We need Equation (14.7) for this part.

For  $[I]_0 = 0.60 M$ ,

$$\begin{aligned} t_{\frac{1}{2}} &= \frac{1}{k[A]_0} \\ &= \frac{1}{(7.0 \times 10^9/M \cdot s)(0.60 M)} \\ &= 2.4 \times 10^{-10} \text{ s} \end{aligned}$$

For  $[I]_0 = 0.42 M$ ,

$$\begin{aligned} t_{\frac{1}{2}} &= \frac{1}{(7.0 \times 10^9/M \cdot s)(0.42 M)} \\ &= 3.4 \times 10^{-10} \text{ s} \end{aligned}$$

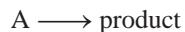
**Check** These results confirm that the half-life of a second-order reaction, unlike that of a first-order reaction, is not a constant but depends on the initial concentration of the reactant(s).

**Similar problem:** 14.26.

**Practice Exercise** The reaction  $2A \longrightarrow B$  is second order with a rate constant of  $51/M \cdot \text{min}$  at  $24^\circ\text{C}$ . (a) Starting with  $[A]_0 = 0.0092 M$ , how long will it take for  $[A]_t = 3.7 \times 10^{-3} M$ ? (b) Calculate the half-life of the reaction.

## Zero-Order Reactions

First- and second-order reactions are the most common reaction types. Reactions whose order is zero are rare. For a zero-order reaction



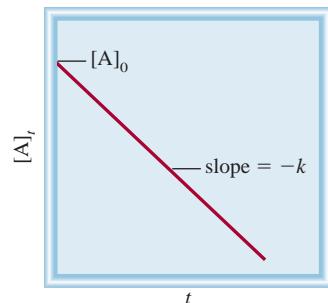
the rate law is given by

$$\begin{aligned} \text{rate} &= k[A]^0 \\ &= k \end{aligned}$$

Thus, the rate of a zero-order reaction is a *constant*, independent of reactant concentration. Using calculus, we can show that

$$[A]_t = -kt + [A]_0 \quad (14.8)$$

Equation (14.8) has the form of a linear equation. As Figure 14.11 shows, a plot of  $[A]_t$  versus  $t$  gives a straight line with slope  $= -k$  and  $y$  intercept  $= [A]_0$ . To calculate the half-life of a zero-order reaction, we set  $[A]_t = [A]_0/2$  in Equation (14.8) and obtain



**Figure 14.11**

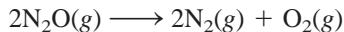
A plot of  $[A]_t$  versus  $t$  for a zero-order reaction. The slope of the line is equal to  $-k$ .

$$t_{\frac{1}{2}} = \frac{[A]_0}{2k} \quad (14.9)$$

**TABLE 14.2****Summary of the Kinetics of Zero-Order, First-Order, and Second-Order Reactions**

| Order | Rate Law        | Concentration-Time Equation              | Half-Life          |
|-------|-----------------|--|--------------------|
| 0     | Rate = $k$      | $[A]_t = -kt + [A]_0$                    | $\frac{[A]_0}{2k}$ |
| 1     | Rate = $k[A]$   | $\ln \frac{[A]_t}{[A]_0} = -kt$          | $\frac{0.693}{k}$  |
| 2     | Rate = $k[A]^2$ | $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ | $\frac{1}{k[A]_0}$ |

Many of the known zero-order reactions take place on a metal surface. An example is the decomposition of nitrous oxide ( $N_2O$ ) to nitrogen and oxygen in the presence of platinum (Pt):



When all the binding sites on Pt are occupied, the rate becomes constant regardless of the amount of  $N_2O$  present in the gas phase. As we will see in Section 14.6, another well-studied zero-order reaction occurs in enzyme catalysis.

Third-order and higher order reactions are quite complex; they are not presented in this book. Table 14.2 summarizes the kinetics of zero-order, first-order, and second-order reactions.

## 14.4 Activation Energy and Temperature Dependence of Rate Constants

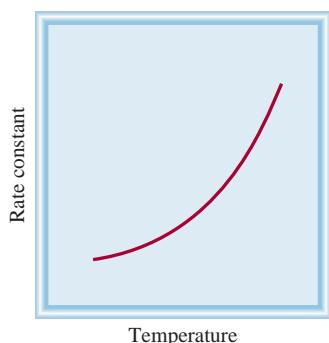
With very few exceptions, reaction rates increase with increasing temperature. For example, much less time is required to hard-boil an egg at  $100^\circ\text{C}$  (about 10 min) than at  $80^\circ\text{C}$  (about 30 min). Conversely, an effective way to preserve foods is to store them at subzero temperatures, thereby slowing the rate of bacterial decay. Figure 14.12 shows a typical example of the relationship between the rate constant of a reaction and temperature. To explain this behavior, we must ask how reactions get started in the first place.

### The Collision Theory of Chemical Kinetics

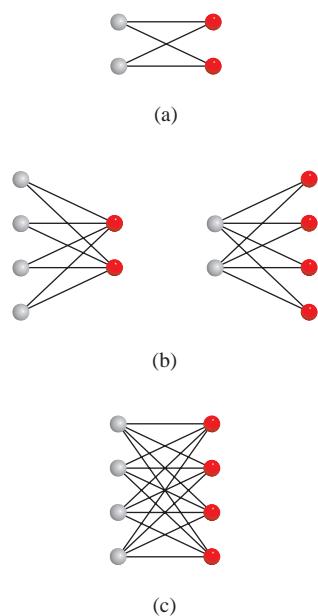
The kinetic molecular theory of gases (p. 153) states that gas molecules frequently collide with one another. Therefore it seems logical to assume—and it is generally true—that chemical reactions occur as a result of collisions between reacting molecules. In terms of the *collision theory* of chemical kinetics, then, we expect the rate of a reaction to be directly proportional to the number of molecular collisions per second, or to the frequency of molecular collisions:

$$\text{rate} \propto \frac{\text{number of collisions}}{\text{s}}$$

This simple relationship explains the dependence of reaction rate on concentration.



**Figure 14.12**  
Dependence of rate constant on temperature. The rate constants of most reactions increase with increasing temperature.



**Figure 14.13**  
Dependence of number of collisions on concentration. We consider here only A-B collisions, which can lead to formation of products. (a) There are four possible collisions among two A and two B molecules. (b) Doubling the number of either type of molecule (but not both) increases the number of collisions to eight. (c) Doubling both the A and B molecules increases the number of collisions to sixteen.



**Animation:**  
Activation Energy  
ARIS, Animations

Consider the reaction of A molecules with B molecules to form some product. Suppose that each product molecule is formed by the direct combination of an A molecule and a B molecule. If we doubled the concentration of A, say, then the number of A-B collisions would also double, because, in any given volume, there would be twice as many A molecules that could collide with B molecules (Figure 14.13). Consequently, the rate would increase by a factor of 2. Similarly, doubling the concentration of B molecules would increase the rate twofold. Thus, we can express the rate law as

$$\text{rate} = k[\text{A}][\text{B}]$$

The reaction is first order in both A and B and obeys second-order kinetics.

The collision theory is intuitively appealing, but the relationship between rate and molecular collisions is more complicated than you might expect. The implication of the collision theory is that a reaction always occurs when an A and a B molecule collide. However, not all collisions lead to reactions. Calculations based on the kinetic molecular theory show that, at ordinary pressures (say, 1 atm) and temperatures (say, 298 K), there are about  $1 \times 10^{27}$  binary collisions (collisions between two molecules) in 1 mL of volume every second, in the gas phase. Even more collisions per second occur in liquids. If every binary collision led to a product, then most reactions would be complete almost instantaneously. In practice, we find that the rates of reactions differ greatly. This means that, in many cases, collisions alone do not guarantee that a reaction will take place.

Any molecule in motion possesses kinetic energy; the faster it moves, the greater the kinetic energy. When molecules collide, part of their kinetic energy is converted to vibrational energy. If the initial kinetic energies are large, then the colliding molecules will vibrate so strongly as to break some of the chemical bonds. This bond fracture is the first step toward product formation. If the initial kinetic energies are small, the molecules will merely bounce off each other intact. Energetically speaking, there is some minimum collision energy below which no reaction occurs.

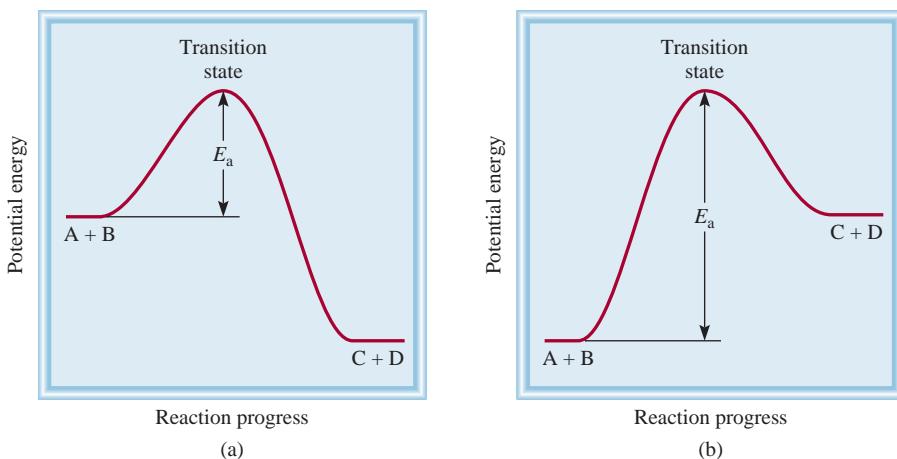
We postulate that, to react, the colliding molecules must have a total kinetic energy equal to or greater than the **activation energy ( $E_a$ )**, which is the minimum amount of energy required to initiate a chemical reaction. Lacking this energy, the molecules remain intact, and no change results from the collision. The species temporarily formed by the reactant molecules as a result of the collision before they form the product is called the **activated complex** (also called the **transition state**).

Figure 14.14 shows two different potential energy profiles for the reaction



If the products are more stable than the reactants, then the reaction will be accompanied by a release of heat; that is, the reaction is exothermic [Figure 14.14(a)]. On the other hand, if the products are less stable than the reactants, then heat will be absorbed by the reacting mixture from the surroundings and we have an endothermic reaction [Figure 14.14(b)]. In both cases, we plot the potential energy of the reacting system versus the progress of the reaction. Qualitatively, these plots show the potential energy changes as reactants are converted to products.

We can think of activation energy as a barrier that prevents less energetic molecules from reacting. Because the number of reactant molecules in an ordinary reaction is very large, the speeds, and hence also the kinetic energies of the molecules, vary greatly. Normally, only a small fraction of the colliding molecules—the fastest-moving ones—have enough kinetic energy to exceed the activation energy. These molecules can therefore take part in the reaction. The increase in the rate (or the rate

**Figure 14.14**

Potential energy profiles for (a) exothermic and (b) endothermic reactions. These plots show the change in potential energy as reactants  $A$  and  $B$  are converted to products  $C$  and  $D$ . The transition state is a highly unstable species with a high potential energy. The activation energy is defined for the forward reaction in both (a) and (b). Note that the products  $C$  and  $D$  are more stable than the reactants in (a) and less stable than those in (b).

constant) with temperature can now be explained: The speeds of the molecules obey the Maxwell distributions shown in Figure 5.15. Compare the speed distributions at two different temperatures. Because more high-energy molecules are present at the higher temperature, the rate of product formation is also greater at the higher temperature.

## The Arrhenius Equation

The dependence of the rate constant of a reaction on temperature can be expressed by this equation, now known as the *Arrhenius equation*:

$$k = Ae^{-E_a/RT} \quad (14.10)$$

in which  $E_a$  is the activation energy of the reaction (in kilojoules per mole),  $R$  is the gas constant ( $8.314 \text{ J/K} \cdot \text{mol}$ ),  $T$  is the absolute temperature, and  $e$  is the base of the natural logarithm scale (see Appendix 3). The quantity  $A$  represents the collision frequency and is called the *frequency factor*. It can be treated as a constant for a given reacting system over a fairly wide temperature range. Equation (14.10) shows that the rate constant is directly proportional to  $A$  and, therefore, to the collision frequency. Further, because of the minus sign associated with the exponent  $E_a/RT$ , the rate constant decreases with increasing activation energy and increases with increasing temperature. This equation can be expressed in a more useful form by taking the natural logarithm of both sides:

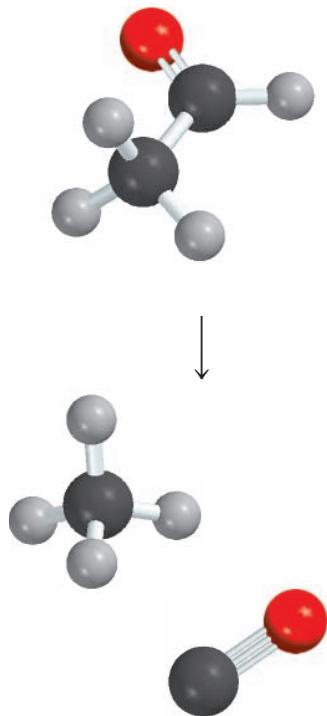
$$\begin{aligned} \ln k &= \ln Ae^{-E_a/RT} \\ \ln k &= \ln A - \frac{E_a}{RT} \end{aligned} \quad (14.11)$$

Equation (14.11) can take the form of a linear equation:

$$\ln k = \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \quad (14.12)$$

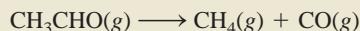
$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow$   
 $y = m x + b$

Thus, a plot of  $\ln k$  versus  $1/T$  gives a straight line whose slope  $m$  is equal to  $-E_a/R$  and whose intercept  $b$  with the ordinate (the  $y$ -axis) is  $\ln A$ .



### Example 14.7

The rate constants for the decomposition of acetaldehyde



were measured at five different temperatures. The data are shown in the table. Plot  $\ln k$  versus  $1/T$ , and determine the activation energy (in kJ/mol) for the reaction. This reaction has been experimentally shown to be “ $\frac{3}{2}$ ” order in CH<sub>3</sub>CHO, so  $k$  has the units of  $1/M^{\frac{1}{2}} \cdot \text{s}$ .

| $k (1/M^{\frac{1}{2}} \cdot \text{s})$ | $T (\text{K})$ |
|--|----------------|
| 0.011                                  | 700            |
| 0.035                                  | 730            |
| 0.105                                  | 760            |
| 0.343                                  | 790            |
| 0.789                                  | 810            |

**Strategy** Consider the Arrhenius equation written as a linear equation

$$\ln k = \left( -\frac{E_a}{R} \right) \left( \frac{1}{T} \right) + \ln A$$

A plot of  $\ln k$  versus  $1/T$  ( $y$  versus  $x$ ) will produce a straight line with a slope equal to  $-E_a/R$ . Thus, the activation energy can be determined from the slope of the plot.

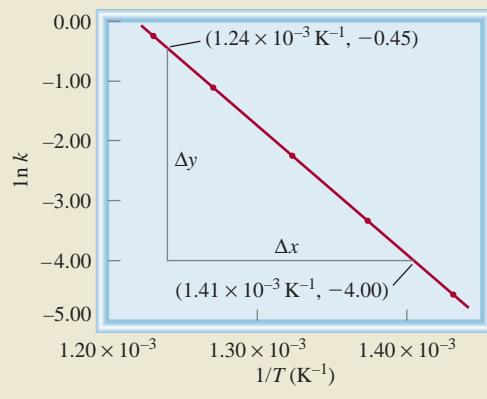
**Solution** First, we convert the data to the following table:

| $\ln k$ | $1/T (\text{K}^{-1})$ |
|---------|-----------------------|
| -4.51   | $1.43 \times 10^{-3}$ |
| -3.35   | $1.37 \times 10^{-3}$ |
| -2.254  | $1.32 \times 10^{-3}$ |
| -1.070  | $1.27 \times 10^{-3}$ |
| -0.237  | $1.23 \times 10^{-3}$ |

A plot of these data yields the graph in Figure 14.15. The slope of the line is calculated from two pairs of coordinates:

$$\text{slope} = \frac{-4.00 - (-0.45)}{(1.41 - 1.24) \times 10^{-3} \text{ K}^{-1}} = -2.09 \times 10^4 \text{ K}$$

**Figure 14.15**  
Plot of  $\ln k$  versus  $1/T$ .



(Continued)

From the linear form of Equation (14.12)

$$\begin{aligned}\text{slope} &= -\frac{E_a}{R} = -2.09 \times 10^4 \text{ K} \\ E_a &= (8.314 \text{ J/K} \cdot \text{mol})(2.09 \times 10^4 \text{ K}) \\ &= 1.74 \times 10^5 \text{ J/mol} \\ &= 1.74 \times 10^2 \text{ kJ/mol}\end{aligned}$$

**Check** It is important to note that although the rate constant itself has the units  $1/M^{1/2} \cdot \text{s}$ , the quantity  $\ln k$  has no units (we cannot take the logarithm of a unit).

**Similar problem:** 14.33.

**Practice Exercise** The second-order rate constant for the decomposition of nitrous oxide ( $\text{N}_2\text{O}$ ) into nitrogen molecule and oxygen atom has been measured at different temperatures:

| $k$ (1/ $M \cdot \text{s}$ ) | $t$ (°C) |
|------------------------------|----------|
| $1.87 \times 10^{-3}$        | 600      |
| 0.0113                       | 650      |
| 0.0569                       | 700      |

Determine graphically the activation energy for the reaction.

An equation relating the rate constants  $k_1$  and  $k_2$  at temperatures  $T_1$  and  $T_2$  can be used to calculate the activation energy or to find the rate constant at another temperature if the activation energy is known. To derive such an equation we start with Equation (14.11):

$$\begin{aligned}\ln k_1 &= \ln A - \frac{E_a}{RT_1} \\ \ln k_2 &= \ln A - \frac{E_a}{RT_2}\end{aligned}$$

Subtracting  $\ln k_2$  from  $\ln k_1$  gives

$$\begin{aligned}\ln k_1 - \ln k_2 &= \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \\ \ln \frac{k_1}{k_2} &= \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \\ \ln \frac{k_1}{k_2} &= \frac{E_a}{R} \left( \frac{T_1 - T_2}{T_1 T_2} \right)\end{aligned}\tag{14.13}$$

### Example 14.8

The rate constant of a first-order reaction is  $3.46 \times 10^{-2} \text{ s}^{-1}$  at 298 K. What is the rate constant at 350 K if the activation energy for the reaction is 50.2 kJ/mol?

**Strategy** A modified form of the Arrhenius equation relates two rate constants at two different temperatures [see Equation (14.13)]. Make sure the units of  $R$  and  $E_a$  are consistent.

**Solution** The data are

$$\begin{array}{ll}k_1 = 3.46 \times 10^{-2} \text{ s}^{-1} & k_2 = ? \\ T_1 = 298 \text{ K} & T_2 = 350 \text{ K}\end{array}$$

(Continued)

Substituting in Equation (14.13),

$$\ln \frac{3.46 \times 10^{-2} \text{ s}^{-1}}{k_2} = \frac{50.2 \times 10^3 \text{ J/mol}}{8.314 \text{ J/K} \cdot \text{mol}} \left[ \frac{298 \text{ K} - 350 \text{ K}}{(298 \text{ K})(350 \text{ K})} \right]$$

We convert  $E_a$  to units of J/mol to match the units of  $R$ . Solving the equation gives

$$\begin{aligned} \ln \frac{3.46 \times 10^{-2} \text{ s}^{-1}}{k_2} &= -3.01 \\ \frac{3.46 \times 10^{-2} \text{ s}^{-1}}{k_2} &= e^{-3.01} = 0.0493 \\ k_2 &= 0.702 \text{ s}^{-1} \end{aligned}$$

**Check** The rate constant is expected to be greater at a higher temperature. Therefore, the answer is reasonable.

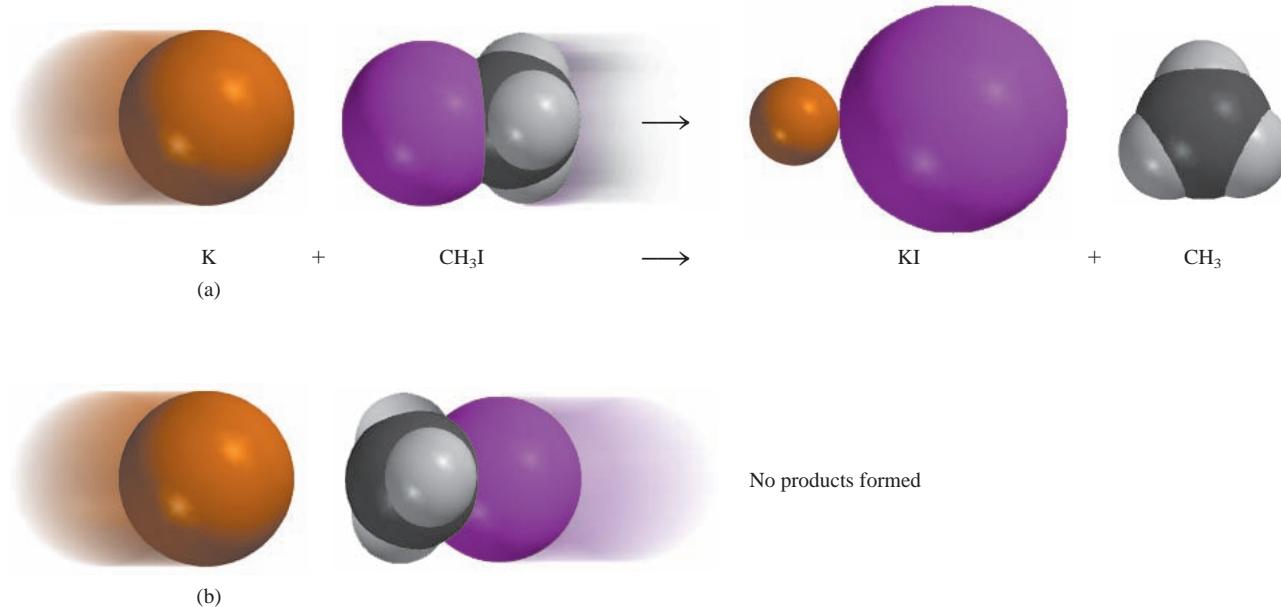
**Similar problem:** 14.36.

**Practice Exercise** The first-order rate constant for the reaction of methyl chloride ( $\text{CH}_3\text{Cl}$ ) with water to produce methanol ( $\text{CH}_3\text{OH}$ ) and hydrochloric acid ( $\text{HCl}$ ) is  $3.32 \times 10^{-10} \text{ s}^{-1}$  at  $25^\circ\text{C}$ . Calculate the rate constant at  $40^\circ\text{C}$  if the activation energy is 116 kJ/mol.



**Animation:**  
Orientation of Collision  
ARIS, Animations

For simple reactions (for example, those between atoms), we can equate the frequency factor ( $A$ ) in the Arrhenius equation with the frequency of collisions between the reacting species. For more complex reactions, we must also consider the “orientation factor,” that is, how reacting molecules are oriented relative to each other. The carefully studied reaction between potassium atoms (K) and methyl iodide ( $\text{CH}_3\text{I}$ ) to form potassium iodide (KI) and a methyl radical ( $\text{CH}_3$ ) illustrates this point:



**Figure 14.16**

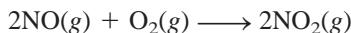
*Relative orientation of reacting molecules. Only when the K atom collides directly with the I atom will the reaction most likely occur.*

This reaction is most favorable only when the K atom collides head-on with the I atom in  $\text{CH}_3\text{I}$  (Figure 14.16). Otherwise, a few or no products are formed. The nature of the orientation factor is satisfactorily dealt with in a more advanced treatment of chemical kinetics.

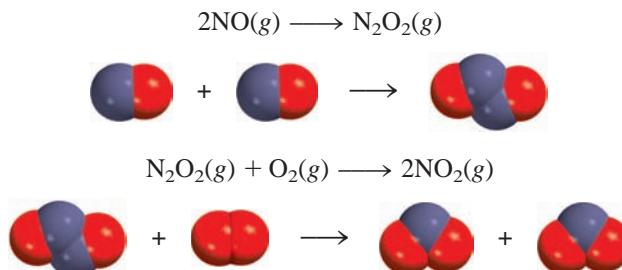
## 14.5 Reaction Mechanisms

As we mentioned earlier, an overall balanced chemical equation does not tell us much about how a reaction actually takes place. In many cases, it merely represents the sum of several *elementary steps*, or *elementary reactions*, *a series of simple reactions that represent the progress of the overall reaction at the molecular level*. The term for the sequence of elementary steps that leads to product formation is **reaction mechanism**. The reaction mechanism is comparable to the route of travel followed during a trip; the overall chemical equation specifies only the origin and destination.

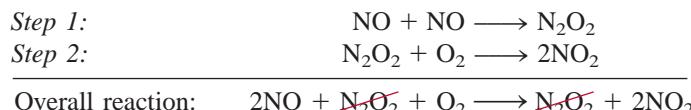
As an example of a reaction mechanism, let us consider the reaction between nitric oxide and oxygen:



We know that the products are not formed directly from the collision of two NO molecules with an  $\text{O}_2$  molecule because  $\text{N}_2\text{O}_2$  is detected during the course of the reaction. Let us assume that the reaction actually takes place via two elementary steps as follows:



In the first elementary step, two NO molecules collide to form a  $\text{N}_2\text{O}_2$  molecule. This event is followed by the reaction between  $\text{N}_2\text{O}_2$  and  $\text{O}_2$  to give two molecules of  $\text{NO}_2$ . The net chemical equation, which represents the overall change, is given by the sum of the elementary steps:



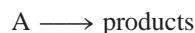
The sum of the elementary steps must give the overall balanced equation.

Species such as  $\text{N}_2\text{O}_2$  are called **intermediates** because they appear in the mechanism of the reaction (that is, the elementary steps) but not in the overall balanced equation. Keep in mind that an intermediate is always formed in an early elementary step and consumed in a later elementary step.

The **molecularity of a reaction** is the number of molecules reacting in an elementary step. These molecules may be of the same or different types. Each of the elementary steps just discussed is called a **bimolecular reaction**, an elementary step that involves two molecules. An example of a **unimolecular reaction**, an elementary step in which only one reacting molecule participates, is the conversion of cyclopropane to propene discussed in Example 14.4. Very few **termolecular reactions**, reactions that involve the participation of three molecules in one elementary step, are known, because the simultaneous encounter of three molecules is a far less likely event than a bimolecular collision.

## Rate Laws and Elementary Steps

Knowing the elementary steps of a reaction enables us to deduce the rate law. Suppose we have the following elementary reaction:



Because there is only one molecule present, this is a unimolecular reaction. It follows that the larger the number of A molecules present, the faster the rate of product formation. Thus, the rate of a unimolecular reaction is directly proportional to the concentration of A, or is first order in A:

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

For a bimolecular elementary reaction involving A and B molecules,



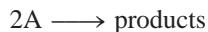
the rate of product formation depends on how frequently A and B collide, which in turn depends on the concentrations of A and B. Thus, we can express the rate as

$$\text{rate} = k[\text{A}][\text{B}]$$

Similarly, for a bimolecular elementary reaction of the type



or



the rate becomes

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

The preceding examples show that the reaction order for each reactant in an elementary reaction is equal to its stoichiometric coefficient in the chemical equation for that step. In general, we cannot tell by merely looking at the overall balanced equation whether the reaction occurs as shown or in a series of steps. This determination is made in the laboratory.

When we study a reaction that has more than one elementary step, the rate law for the overall process is given by the **rate-determining step**, which is *the slowest step in the sequence of steps leading to product formation*.

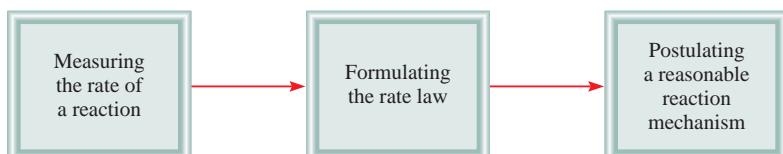
An analogy for the rate-determining step is the flow of traffic along a narrow road. Assuming the cars cannot pass one another on the road, the rate at which the cars travel is governed by the slowest-moving car.

Experimental studies of reaction mechanisms begin with the collection of data (rate measurements). Next, we analyze the data to determine the rate constant and order of the reaction, and we write the rate law. Finally, we suggest a plausible mechanism for the reaction in terms of elementary steps (Figure 14.17). The elementary steps must satisfy two requirements:



**Interactivity:**  
Mechanisms and Rates  
ARIS, Interactives

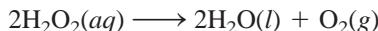
**Figure 14.17**  
*Sequence of steps in the study of a reaction mechanism.*



- The sum of the elementary steps must give the overall balanced equation for the reaction.
- The rate-determining step should predict the same rate law as is determined experimentally.

Remember that for a proposed reaction scheme, we must be able to detect the presence of any intermediate(s) formed in one or more elementary steps.

The decomposition of hydrogen peroxide illustrates the elucidation of reaction mechanisms by experimental studies. This reaction is facilitated by iodide ions ( $I^-$ ) (Figure 14.18). The overall reaction is

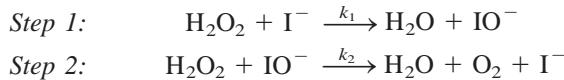


By experiment, the rate law is found to be

$$\text{rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$$

Thus, the reaction is first order with respect to both  $\text{H}_2\text{O}_2$  and  $\text{I}^-$ . You can see that decomposition does not occur in a single elementary step corresponding to the overall balanced equation. If it did, the reaction would be second order in  $\text{H}_2\text{O}_2$  (note the coefficient 2 in the equation). What's more, the  $\text{I}^-$  ion, which is not even in the overall equation, appears in the rate law expression. How can we reconcile these facts?

We can account for the observed rate law by assuming that the reaction takes place in two separate elementary steps, each of which is bimolecular:



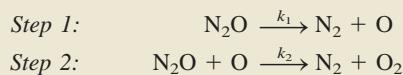
If we further assume that step 1 is the rate-determining step, then the rate of the reaction can be determined from the first step alone:

$$\text{rate} = k_1[\text{H}_2\text{O}_2][\text{I}^-]$$

where  $k_1 = k$ . Note that the  $\text{IO}^-$  ion is an intermediate because it does not appear in the overall balanced equation. Although the  $\text{I}^-$  ion also does not appear in the overall equation,  $\text{I}^-$  differs from  $\text{IO}^-$  in that the former is present at the start of the reaction and at its completion. The function of  $\text{I}^-$  is to speed up the reaction—that is, it is a *catalyst*. We will discuss catalysis in Section 14.6. Figure 14.19 shows the potential energy profile for a reaction like the decomposition of  $\text{H}_2\text{O}_2$ . We see that the first step, which is rate determining, has a larger activation energy than the second step. The intermediate, although stable enough to be observed, reacts quickly to form the products.

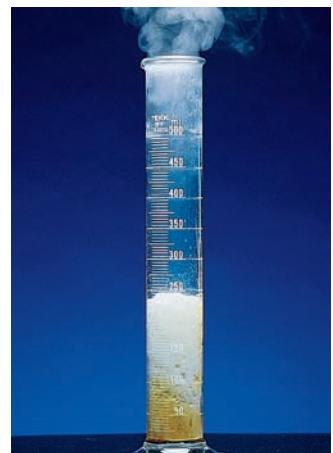
### Example 14.9

The gas-phase decomposition of nitrous oxide ( $\text{N}_2\text{O}$ ) is believed to occur via two elementary steps:



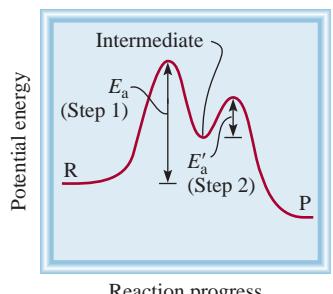
Experimentally the rate law is found to be  $\text{rate} = k[\text{N}_2\text{O}]$ . (a) Write the equation for the overall reaction. (b) Identify the intermediates. (c) What can you say about the relative rates of steps 1 and 2?

(Continued)



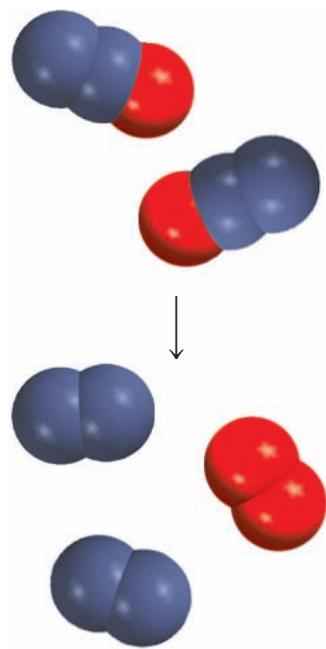
**Figure 14.18**

The decomposition of hydrogen peroxide is catalyzed by the iodide ion. A few drops of liquid soap have been added to the solution to dramatize the evolution of oxygen gas. (Some of the iodide ions are oxidized to molecular iodine, which then reacts with iodide ions to form the brown triiodide ion,  $\text{I}_3^-$ .)



**Figure 14.19**

Potential energy profile for a two-step reaction in which the first step is rate-determining.  $R$  and  $P$  represent reactants and products, respectively.



**Similar problem:** 14.47.

**Strategy** (a) Because the overall reaction can be broken down into elementary steps, knowing the elementary steps would enable us to write the overall reaction. (b) What are the characteristics of an intermediate? Does it appear in the overall reaction? (c) What determines which elementary step is rate determining? How does a knowledge of the rate-determining step help us write the rate law of a reaction?

**Solution** (a) Adding the equations for steps 1 and 2 gives the overall reaction:



(b) Because the O atom is produced in the first elementary step and it does not appear in the overall balanced equation, it is an intermediate.

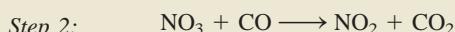
(c) If we assume that step 1 is the rate-determining step (that is, if  $k_2 \gg k_1$ ), then the rate of the overall reaction is given by

$$\text{rate} = k_1[\text{N}_2\text{O}]$$

$$\text{and } k = k_1.$$

**Check** Step 1 must be the rate-determining step because the rate law written from this step matches the experimentally determined rate law, that is,  $\text{rate} = k[\text{N}_2\text{O}]$ .

**Practice Exercise** The reaction between  $\text{NO}_2$  and CO to produce NO and  $\text{CO}_2$  is believed to occur via two steps:



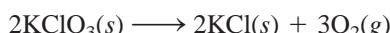
The experimental rate law is  $\text{rate} = k[\text{NO}_2]^2$ . (a) Write the equation for the overall reaction. (b) Identify the intermediate. (c) What can you say about the relative rates of steps 1 and 2?

## 14.6 Catalysis

A rise in temperature also increases the rate of a reaction. However, at high temperatures, the products formed may undergo other reactions, thereby reducing the yield.

We saw in studying the decomposition of hydrogen peroxide that the reaction rate depends on the concentration of iodide ions even though  $\text{I}^-$  does not appear in the overall equation. We noted there that  $\text{I}^-$  acts as a catalyst for that reaction. A **catalyst** is a substance that increases the rate of a chemical reaction by providing an alternate reaction pathway without itself being consumed. The catalyst may react to form an intermediate, but it is regenerated in a subsequent step of the reaction.

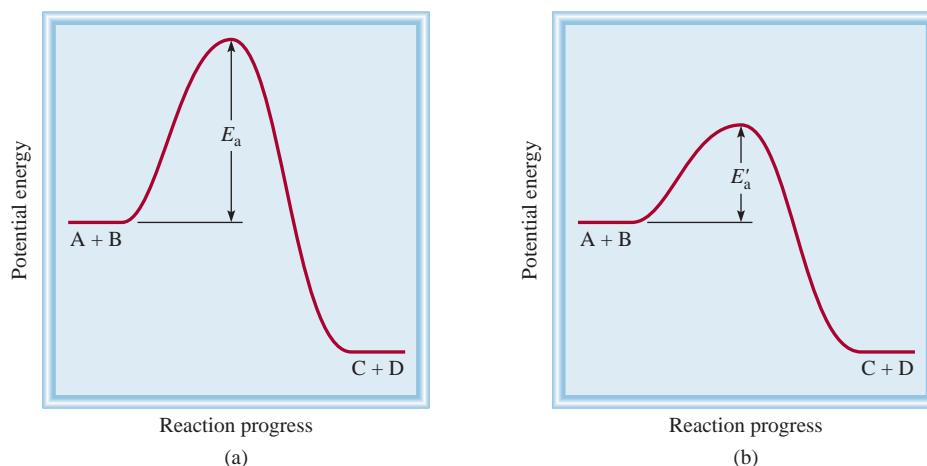
In the laboratory preparation of molecular oxygen, a sample of potassium chlorate is heated; the reaction is (see p. 151)



However, this thermal decomposition is very slow in the absence of a catalyst. The rate of decomposition can be increased dramatically by adding a small amount of the catalyst manganese dioxide ( $\text{MnO}_2$ ), a black powdery substance. All the  $\text{MnO}_2$  can be recovered at the end of the reaction, just as all the  $\text{I}^-$  ions remain following  $\text{H}_2\text{O}_2$  decomposition.

A catalyst speeds up a reaction by providing a set of elementary steps with more favorable kinetics than those that exist in its absence. From Equation (14.10) we know that the rate constant  $k$  (and hence the rate) of a reaction depends on the frequency factor  $A$  and the activation energy  $E_a$ —the larger the  $A$  or the smaller the  $E_a$ , the

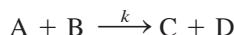
To extend the traffic analogy, adding a catalyst can be compared with building a tunnel through a mountain to connect two towns that were previously linked by a winding road over the mountain.

**Figure 14.20**

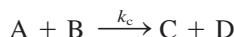
*Comparison of the activation energy barriers of an uncatalyzed reaction and the same reaction with a catalyst. The catalyst lowers the energy barrier but does not affect the actual energies of the reactants or products. Although the reactants and products are the same in both cases, the reaction mechanisms and rate laws are different in (a) and (b).*

greater the rate. In many cases, a catalyst increases the rate by lowering the activation energy for the reaction.

Let us assume that the following reaction has a certain rate constant  $k$  and an activation energy  $E_a$ :



In the presence of a catalyst, however, the rate constant is  $k_c$  (called the *catalytic rate constant*):



By the definition of a catalyst,

$$\text{rate}_{\text{catalyzed}} > \text{rate}_{\text{uncatalyzed}}$$

Figure 14.20 shows the potential energy profiles for both reactions. Note that the total energies of the reactants ( $A$  and  $B$ ) and those of the products ( $C$  and  $D$ ) are unaffected by the catalyst; the only difference between the two is a lowering of the activation energy from  $E_a$  to  $E'_a$ . Because the activation energy for the reverse reaction is also lowered, a catalyst enhances the rate of the reverse reaction to the same extent as it does the forward reaction rate.



**A catalyst lowers the activation energy for both the forward and reverse reactions.**

There are three general types of catalysis, depending on the nature of the rate-increasing substance: heterogeneous catalysis, homogeneous catalysis, and enzyme catalysis.

## Heterogeneous Catalysis

In *heterogeneous catalysis*, the reactants and the catalyst are in different phases. Usually the catalyst is a solid and the reactants are either gases or liquids. Heterogeneous catalysis is by far the most important type of catalysis in industrial chemistry, especially in the synthesis of many key chemicals. Here we describe three specific examples of heterogeneous catalysis.

### The Haber Synthesis of Ammonia

Ammonia is an extremely valuable inorganic substance used in the fertilizer industry, the manufacture of explosives, and many other applications. Around the turn of the

| 1A | 4B | 5B | 6B | 7B | 8B | 1B | 2B | 3A | Al |
|----|----|----|----|----|----|----|----|----|----|
| K  | Ti | V  | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|    | Zr |    | Mg | Ru | Rh | Pd |    |    |    |
|    |    |    | W  | Re | Os | Ir | Pt | Au |    |

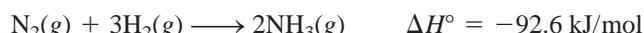
Metals and compounds of metals that are most frequently used in heterogeneous catalysis.

century, many chemists strove to synthesize ammonia from nitrogen and hydrogen. The supply of atmospheric nitrogen is virtually inexhaustible, and hydrogen gas can be produced readily by passing steam over heated coal:



Hydrogen is also a by-product of petroleum refining.

The formation of  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2$  is exothermic:



But the reaction rate is extremely slow at room temperature. To be practical on a large scale, a reaction must occur at an appreciable rate *and* it must have a high yield of the desired product. Raising the temperature does accelerate the preceding reaction, but at the same time it promotes the decomposition of  $\text{NH}_3$  molecules into  $\text{N}_2$  and  $\text{H}_2$ , thus lowering the yield of  $\text{NH}_3$ .

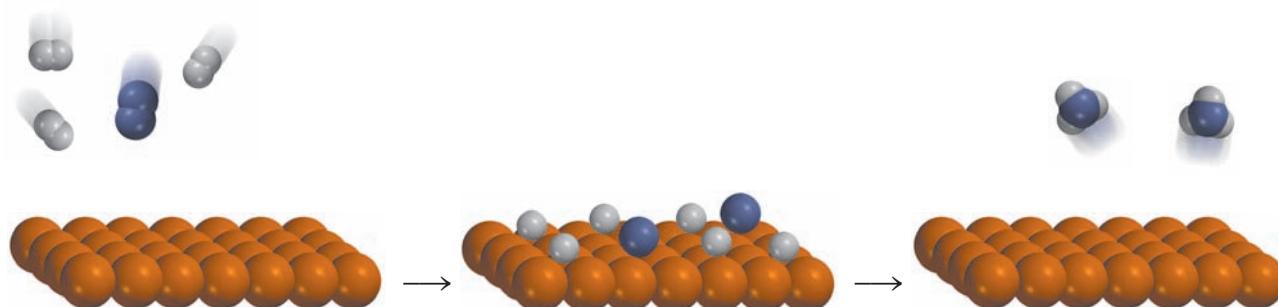
In 1905, after testing literally hundreds of compounds at various temperatures and pressures, the German chemist Fritz Haber discovered that iron plus a few percent of oxides of potassium and aluminum catalyze the reaction of hydrogen with nitrogen to yield ammonia at about  $500^\circ\text{C}$ . This procedure is known as the *Haber process*.

In heterogeneous catalysis, the surface of the solid catalyst is usually the site of the reaction. The initial step in the Haber process involves the dissociation of  $\text{N}_2$  and  $\text{H}_2$  on the metal surface (Figure 14.21). Although the dissociated species are not truly free atoms because they are bonded to the metal surface, they are highly reactive. The two reactant molecules behave very differently on the catalyst surface. Studies show that  $\text{H}_2$  dissociates into atomic hydrogen at temperatures as low as  $-196^\circ\text{C}$  (the boiling point of liquid nitrogen). Nitrogen molecules, on the other hand, dissociate at about  $500^\circ\text{C}$ . The highly reactive N and H atoms combine rapidly at high temperatures to produce the desired  $\text{NH}_3$  molecules:



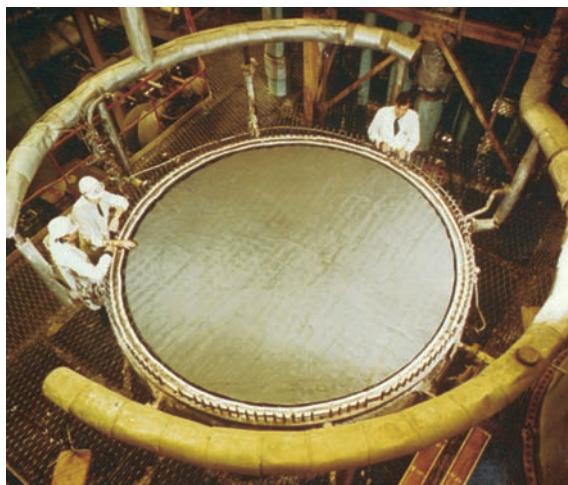
### ***The Manufacture of Nitric Acid***

Nitric acid is one of the most important inorganic acids. It is used in the production of fertilizers, dyes, drugs, and explosives. The major industrial method of producing



**Figure 14.21**

*The catalytic action in the synthesis of ammonia. First the  $\text{H}_2$  and  $\text{N}_2$  molecules bind to the surface of the catalyst. This interaction weakens the covalent bonds within the molecules and eventually causes the molecules to dissociate. The highly reactive H and N atoms combine to form  $\text{NH}_3$  molecules, which then leave the surface.*

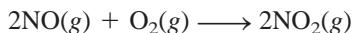


**Figure 14.22**  
Platinum-rhodium catalyst used in the Ostwald process.

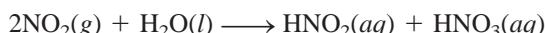
nitric acid is the *Ostwald process*, after the German chemist Wilhelm Ostwald. The starting materials, ammonia and molecular oxygen, are heated in the presence of a platinum-rhodium catalyst (Figure 14.22) to about 800°C:



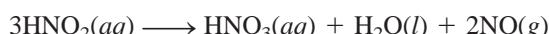
The nitric oxide formed readily oxidizes (without catalysis) to nitrogen dioxide:



When dissolved in water,  $\text{NO}_2$  forms both nitrous acid and nitric acid:



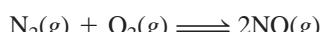
On heating, nitrous acid is converted to nitric acid as follows:



The NO generated can be recycled to produce  $\text{NO}_2$  in the second step.

### Catalytic Converters

At high temperatures inside a running car's engine, nitrogen and oxygen gases react to form nitric oxide:

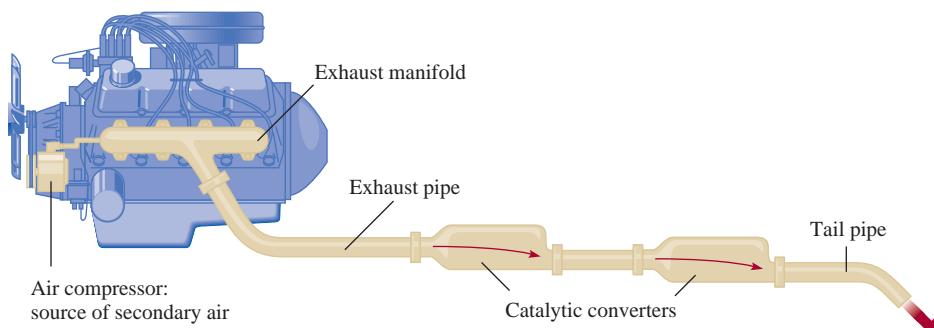


When released into the atmosphere, NO rapidly combines with  $\text{O}_2$  to form  $\text{NO}_2$ . Nitrogen dioxide and other gases emitted by an automobile, such as carbon monoxide (CO) and various unburned hydrocarbons, make automobile exhaust a major source of air pollution.

Most new cars are equipped with catalytic converters (Figure 14.23). An efficient catalytic converter serves two purposes: It oxidizes CO and unburned hydrocarbons to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and it reduces NO and  $\text{NO}_2$  to  $\text{N}_2$  and  $\text{O}_2$ . Hot exhaust gases into which air has been injected are passed through the first chamber of one converter to accelerate the complete burning of hydrocarbons and to decrease CO emission. (A cross section of the catalytic converter, containing Pt or Pd or a transition metal oxide such as  $\text{CuO}$  or  $\text{Cr}_2\text{O}_3$ , is shown in Figure 14.24.) However, because high

**Figure 14.23**

**Figure 1-11**  
A two-stage catalytic converter  
for an automobile.



**Figure 14.24**

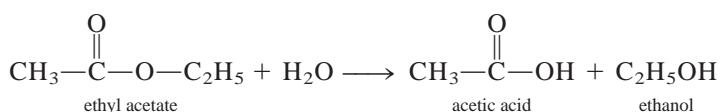
*A cross-sectional view of a catalytic converter. The beads contain platinum, palladium, and rhodium, which catalyze the combustion of CO and hydrocarbons.*

This reaction is zero order in water because water's concentration is very high and therefore it is unaffected by the reaction.

temperatures increase NO production, a second chamber containing a different catalyst (a transition metal or a transition metal oxide) and operating at a lower temperature is required to dissociate NO into N<sub>2</sub> and O<sub>2</sub> before the exhaust is discharged through the tailpipe.

## Homogeneous Catalysis

In *homogeneous catalysis* the reactants and catalyst are dispersed in a single phase, usually liquid. Acid and base catalyses are the most important type of homogeneous catalysis in liquid solution. For example, the reaction of ethyl acetate with water to form acetic acid and ethanol normally occurs too slowly to be measured.



In the absence of the catalyst, the rate law is given by

$$\text{rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5]$$

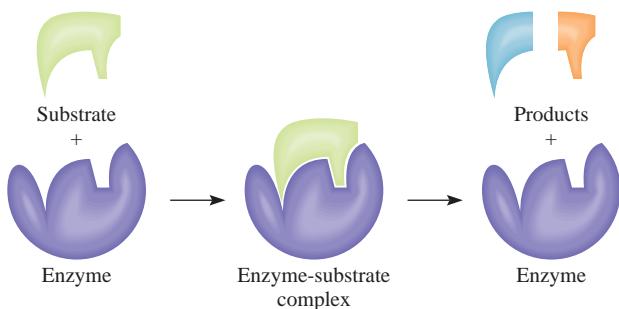
However, the reaction can be catalyzed by an acid. In the presence of hydrochloric acid, the rate is given by

$$\text{rate} = k_c [\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}^+]$$

## Enzyme Catalysis

Of all the intricate processes that have evolved in living systems, none is more striking or more essential than enzyme catalysis. ***Enzymes*** are *biological catalysts*. The amazing fact about enzymes is that not only can they increase the rate of biochemical reactions by factors ranging from  $10^6$  to  $10^{18}$ , but they are also highly specific. An enzyme acts only on certain molecules, called *substrates* (that is, reactants), while leaving the rest of the system unaffected. It has been estimated that an average living cell may contain some 3000 different enzymes, each of them catalyzing a specific reaction in which a substrate is converted into the appropriate products. Enzyme catalyses are usually homogeneous with the substrate and enzyme present in the same aqueous solution.

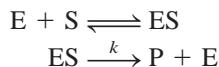
An enzyme is typically a large protein molecule that contains one or more *active sites* where interactions with substrates take place. These sites are structurally compatible with specific molecules, in much the same way as a key fits a particular lock.

**Figure 14.25**

*The lock-and-key model of an enzyme's specificity for substrate molecules.*

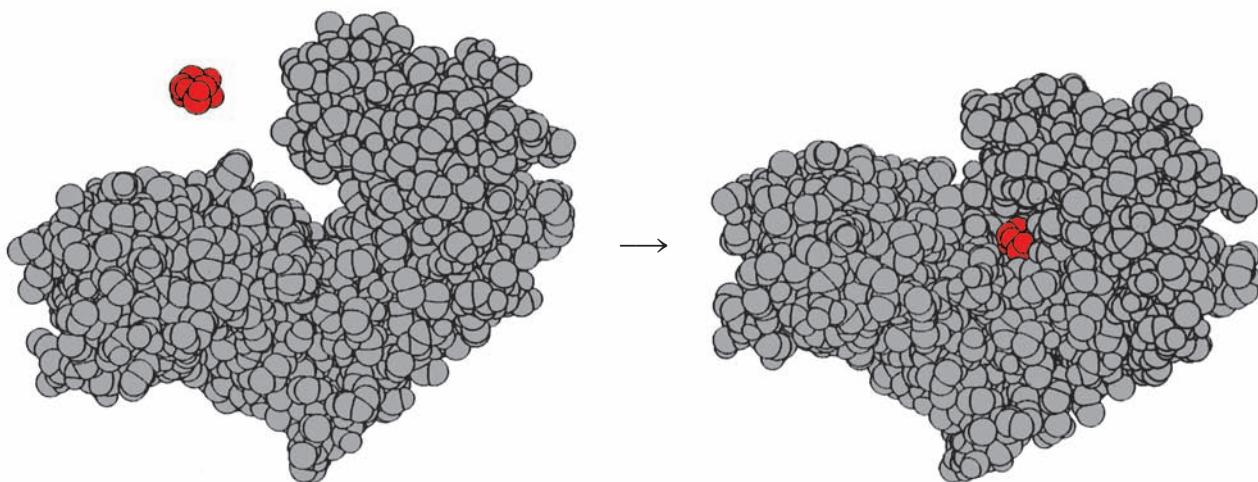
(Figure 14.25). However, an enzyme molecule (or at least its active site) has a fair amount of structural flexibility and can modify its shape to accommodate different kinds of substrates (Figure 14.26).

The mathematical treatment of enzyme kinetics is quite complex, even when we know the basic steps involved in the reaction. A simplified scheme is



in which E, S, and P represent enzyme, substrate, and product, and ES is the enzyme-substrate intermediate. Figure 14.27 shows the potential energy profile for the reaction. It is often assumed that the formation of ES and its decomposition back to enzyme and substrate molecules occur rapidly and that the rate-determining step is the formation of product. In general, the rate of such a reaction is given by the equation

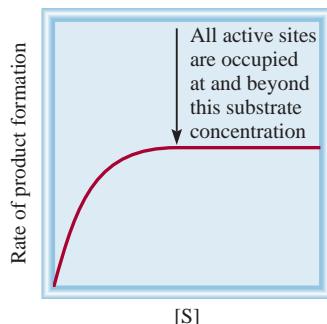
$$\begin{aligned} \text{rate} &= \frac{\Delta[P]}{\Delta t} \\ &= k[ES] \end{aligned}$$

**Figure 14.26**

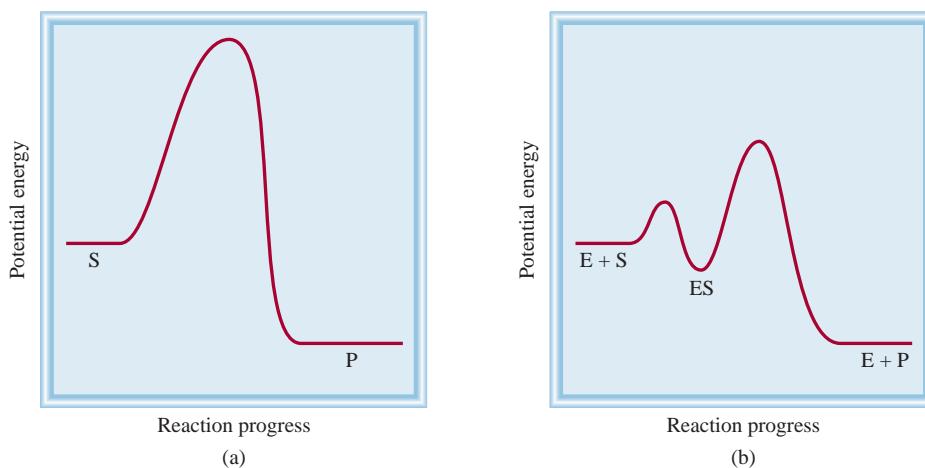
*Left to right: The binding of glucose molecule (red) to hexokinase (an enzyme in the metabolic pathway). Note how the region at the active site closes around glucose after binding. Frequently, the geometries of both the substrate and the active site are altered to fit each other.*

**Figure 14.27**

Comparison of (a) an uncatalyzed reaction and (b) the same reaction catalyzed by an enzyme. The plot in (b) assumes that the catalyzed reaction has a two-step mechanism, in which the second step ( $ES \rightarrow E + P$ ) is rate-determining.

**Figure 14.28**

Plot of the rate of product formation versus substrate concentration in an enzyme-catalyzed reaction.



The concentration of the  $ES$  intermediate is itself proportional to the amount of the substrate present, and a plot of the rate versus the concentration of substrate typically yields a curve such as that shown in Figure 14.28. Initially the rate rises rapidly with increasing substrate concentration. However, above a certain concentration all the active sites are occupied, and the reaction becomes zero order in the substrate. That is, the rate remains the same even though the substrate concentration increases. At and beyond this point, the rate of formation of product depends only on how fast the  $ES$  intermediate breaks down, not on the number of substrate molecules present.

## KEY EQUATIONS

$$\text{rate} = k[A]^x[B]^y \quad (14.1)$$

Rate law expressions. The sum  $(x + y)$  gives the overall order of the reaction.

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad (14.3)$$

Relationship between concentration and time for a first-order reaction.

$$\ln [A]_t = -kt + \ln [A]_0 \quad (14.4)$$

Equation for the graphical determination of  $k$  for a first-order reaction.

$$t_{\frac{1}{2}} = \frac{0.693}{k} \quad (14.5)$$

Half-life for a first-order reaction.

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \quad (14.6)$$

Relationship between concentration and time for a second-order reaction.

$$[A]_t = -kt + [A]_0 \quad (14.8)$$

Relationship between concentration and time for a zero-order reaction.

$$k = Ae^{-E_a/RT} \quad (14.10)$$

The Arrhenius equation expressing the dependence of the rate constant on activation energy and temperature.

$$\ln k = \left( -\frac{E_a}{R} \right) \left( \frac{1}{T} \right) + \ln A \quad (14.12)$$

Equation for the graphical determination of activation energy.

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{T_1 - T_2}{T_1 T_2} \right) \quad (14.13)$$

Relationships of rate constants at two different temperatures.

## SUMMARY OF FACTS AND CONCEPTS

- The rate of a chemical reaction is the change in the concentration of reactants or products over time. The rate is not constant, but varies continuously as concentrations change.
- The rate law expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to appropriate powers. The rate constant  $k$  for a given reaction changes only with temperature.
- Reaction order is the power to which the concentration of a given reactant is raised in the rate law. Overall reaction order is the sum of the powers to which reactant concentrations are raised in the rate law. The rate law and the reaction order cannot be determined from the stoichiometry of the overall equation for a reaction; they must be determined by experiment. For a zero-order reaction, the reaction rate is equal to the rate constant.
- The half-life of a reaction (the time it takes for the concentration of a reactant to decrease by one-half) can be used to determine the rate constant of a first-order reaction.
- In terms of collision theory, a reaction occurs when molecules collide with sufficient energy, called the activation energy, to break the bonds and initiate the reaction. The rate constant and the activation energy are related by the Arrhenius equation.
- The overall balanced equation for a reaction may be the sum of a series of simple reactions, called elementary steps. The complete series of elementary steps for a reaction is the reaction mechanism.
- If one step in a reaction mechanism is much slower than all other steps, it is the rate-determining step.
- A catalyst speeds up a reaction usually by lowering the value of  $E_a$ . A catalyst can be recovered unchanged at the end of a reaction.
- In heterogeneous catalysis, which is of great industrial importance, the catalyst is a solid and the reactants are gases or liquids. In homogeneous catalysis, the catalyst and the reactants are in the same phase. Enzymes are catalysts in living systems.

## KEY WORDS

|                                     |   |                               |                               |
|-------------------------------------|---|-------------------------------|-------------------------------|
| Activated complex, p. 472           | Enzyme, p. 484                          | Rate constant ( $k$ ), p. 460 | Second-order reaction, p. 468 |
| Activation energy ( $E_a$ ), p. 472 | First-order reaction, p. 463            | Rate-determining step, p. 478 | Termolecular reaction, p. 477 |
| Bimolecular reaction, p. 477        | Half-life ( $t_{\frac{1}{2}}$ ), p. 466 | Rate law, p. 460              | Transition state, p. 472      |
| Catalyst, p. 480                    | Intermediate, p. 477                    | Reaction mechanism, p. 477    | Unimolecular reaction, p. 477 |
| Chemical kinetics, p. 455           | Molecularity of a reaction, p. 477      | Reaction order, p. 460        |                               |
| Elementary step, p. 477             |   | Reaction rate, p. 455         |                               |

## QUESTIONS AND PROBLEMS

### Reaction Rate

#### Review Questions

- What is meant by the rate of a chemical reaction?
- What are the units of the rate of a reaction?
- What are the advantages of measuring the initial rate of a reaction?
- Can you suggest two reactions that are very slow (take days or longer to complete) and two reactions that are very fast (are over in minutes or seconds)?

#### Problems

- Write the reaction rate expressions for these reactions in terms of the disappearance of the reactants and the appearance of products:
  - $H_2(g) + I_2(g) \longrightarrow 2HI(g)$
  - $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$
  - $5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$
- Consider the reaction
 
$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

Suppose that at a particular moment during the reaction molecular hydrogen is reacting at the rate of  $0.074\text{ M/s}$ . (a) At what rate is ammonia being formed? (b) At what rate is molecular nitrogen reacting?

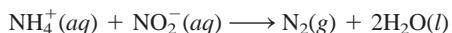
## Rate Laws

### Review Questions

- 14.7 Explain what is meant by the rate law of a reaction.
- 14.8 What is meant by the order of a reaction?
- 14.9 What are the units for the rate constants of first-order and second-order reactions?
- 14.10 Write an equation relating the concentration of a reactant A at  $t = 0$  to that at  $t = t$  for a first-order reaction. Define all the terms and give their units.
- 14.11 Consider the zero-order reaction  $\text{A} \longrightarrow \text{product}$ . (a) Write the rate law for the reaction. (b) What are the units for the rate constant? (c) Plot the rate of the reaction versus  $[\text{A}]$ .
- 14.12 The rate constant of a first-order reaction is  $66\text{ s}^{-1}$ . What is the rate constant in units of minutes?
- 14.13 On which of these quantities does the rate constant of a reaction depend: (a) concentrations of reactants, (b) nature of reactants, (c) temperature?
- 14.14 For each of these pairs of reaction conditions, indicate which has the faster rate of formation of hydrogen gas: (a) sodium or potassium with water, (b) magnesium or iron with  $1.0\text{ M HCl}$ , (c) magnesium rod or magnesium powder with  $1.0\text{ M HCl}$ , (d) magnesium with  $0.10\text{ M HCl}$  or magnesium with  $1.0\text{ M HCl}$ .

### Problems

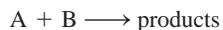
- 14.15 The rate law for the reaction



is given by  $\text{rate} = k[\text{NH}_4^+][\text{NO}_2^-]$ . At  $25^\circ\text{C}$ , the rate constant is  $3.0 \times 10^{-4}/\text{M} \cdot \text{s}$ . Calculate the rate of the reaction at this temperature if  $[\text{NH}_4^+] = 0.26\text{ M}$  and  $[\text{NO}_2^-] = 0.080\text{ M}$ .

- 14.16 Starting with the data in Table 14.1, (a) deduce the rate law for the reaction, (b) calculate the rate constant, and (c) calculate the rate of the reaction at the time when  $[\text{F}_2] = 0.010\text{ M}$  and  $[\text{ClO}_2] = 0.020\text{ M}$ .

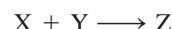
- 14.17 Consider the reaction



From these data obtained at a certain temperature, determine the order of the reaction and calculate the rate constant:

| [A] (M) | [B] (M) | Rate (M/s)            |
|---------|---------|-----------------------|
| 1.50    | 1.50    | $3.20 \times 10^{-1}$ |
| 1.50    | 2.50    | $3.20 \times 10^{-1}$ |
| 3.00    | 1.50    | $6.40 \times 10^{-1}$ |

- 14.18 Consider the reaction



These data are obtained at  $360\text{ K}$ :

| Initial Rate of Disappearance of X (M/s) | [X]  | [Y]  |
|--|------|------|
| 0.147                                    | 0.10 | 0.50 |
| 0.127                                    | 0.20 | 0.30 |
| 4.064                                    | 0.40 | 0.60 |
| 1.016                                    | 0.20 | 0.60 |
| 0.508                                    | 0.40 | 0.30 |

(a) Determine the order of the reaction. (b) Determine the initial rate of disappearance of X when the concentration of X is  $0.30\text{ M}$  and that of Y is  $0.40\text{ M}$ .

- 14.19 Determine the overall orders of the reactions to which these rate laws apply: (a) rate =  $k[\text{NO}_2]^2$ ; (b) rate =  $k$ ; (c) rate =  $k[\text{H}_2][\text{Br}_2]^{\frac{1}{2}}$ ; (d) rate =  $k[\text{NO}]^2[\text{O}_2]$ .

- 14.20 Consider the reaction



The rate of the reaction is  $1.6 \times 10^{-2}\text{ M/s}$  when the concentration of A is  $0.35\text{ M}$ . Calculate the rate constant if the reaction is (a) first order in A, (b) second order in A.

## Relationship Between Reactant Concentration and Time

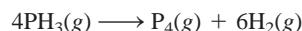
### Review Questions

- 14.21 Define the half-life of a reaction. Write the equation relating the half-life of a first-order reaction to the rate constant.
- 14.22 For a first-order reaction, how long will it take for the concentration of reactant to fall to one-eighth its original value? Express your answer in terms of the half-life ( $t_{\frac{1}{2}}$ ) and in terms of the rate constant  $k$ .

### Problems

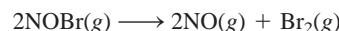
- 14.23 What is the half-life of a compound if 75 percent of a given sample of the compound decomposes in  $60\text{ min}$ ? Assume first-order kinetics.

- 14.24 The thermal decomposition of phosphine ( $\text{PH}_3$ ) into phosphorus and molecular hydrogen is a first-order reaction:



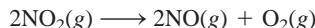
The half-life of the reaction is  $35.0\text{ s}$  at  $680^\circ\text{C}$ . Calculate (a) the first-order rates constant for the reaction and (b) the time required for 95 percent of the phosphine to decompose.

- 14.25 The rate constant for the second-order reaction



is  $0.80/M \cdot s$  at  $10^\circ\text{C}$ . (a) Starting with a concentration of  $0.086\text{ M}$ , calculate the concentration of  $\text{NOBr}$  after 22 s. (b) Calculate the half-lives when  $[\text{NOBr}]_0 = 0.072\text{ M}$  and  $[\text{NOBr}]_0 = 0.054\text{ M}$ .

- 14.26** The rate constant for the second-order reaction



is  $0.54/M \cdot s$  at  $300^\circ\text{C}$ . (a) How long (in seconds) would it take for the concentration of  $\text{NO}_2$  to decrease from  $0.62\text{ M}$  to  $0.28\text{ M}$ ? (b) Calculate the half-lives at these two concentrations.

## Activation Energy

### Review Questions

- 14.27** Define activation energy. What role does activation energy play in chemical kinetics?
- 14.28** Write the Arrhenius equation and define all terms.
- 14.29** Use the Arrhenius equation to show why the rate constant of a reaction (a) decreases with increasing activation energy and (b) increases with increasing temperature.
- 14.30** As we know, methane burns readily in oxygen in a highly exothermic reaction. Yet a mixture of methane and oxygen gas can be kept indefinitely without any apparent change. Explain.
- 14.31** Sketch a potential-energy-versus-reaction-progress plot for the following reactions:
- $\text{S}(s) + \text{O}_2(g) \longrightarrow \text{SO}_2(g)$   
 $\Delta H^\circ = -296.06\text{ kJ/mol}$
  - $\text{Cl}_2(g) \longrightarrow \text{Cl}(g) + \text{Cl}(g)$   
 $\Delta H^\circ = 242.7\text{ kJ/mol}$
- 14.32** The reaction  $\text{H} + \text{H}_2 \longrightarrow \text{H}_2 + \text{H}$  has been studied for many years. Sketch a potential-energy-versus-reaction-progress diagram for this reaction.

### Problems

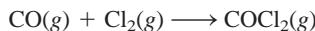
- 14.33** Variation of the rate constant with temperature for the first-order reaction



is given in the following table. Determine graphically the activation energy for the reaction.

| T(K) | $k(\text{s}^{-1})$ |
|------|--------------------|
| 273  | $7.87 \times 10^3$ |
| 298  | $3.46 \times 10^5$ |
| 318  | $4.98 \times 10^6$ |
| 338  | $4.87 \times 10^7$ |

- 14.34** Given the same concentrations, the reaction



at  $250^\circ\text{C}$  is  $1.50 \times 10^3$  times as fast as the same reaction at  $150^\circ\text{C}$ . Calculate the energy of activation for this reaction. Assume that the frequency factor is constant.

- 14.35** For the reaction



the frequency factor  $A$  is  $8.7 \times 10^{12}\text{ s}^{-1}$  and the activation energy is  $63\text{ kJ/mol}$ . What is the rate constant for the reaction at  $75^\circ\text{C}$ ?

- 14.36** The rate constant of a first-order reaction is  $4.60 \times 10^{-4}\text{ s}^{-1}$  at  $350^\circ\text{C}$ . If the activation energy is  $104\text{ kJ/mol}$ , calculate the temperature at which its rate constant is  $8.80 \times 10^{-4}\text{ s}^{-1}$ .

- 14.37** The rate constants of some reactions double with every 10-degree rise in temperature. Assume a reaction takes place at  $295\text{ K}$  and  $305\text{ K}$ . What must the activation energy be for the rate constant to double as described?

- 14.38** The rate at which tree crickets chirp is  $2.0 \times 10^2$  per minute at  $27^\circ\text{C}$  but only  $39.6$  per minute at  $5^\circ\text{C}$ . From these data, calculate the “energy of activation” for the chirping process. (*Hint:* The ratio of rates is equal to the ratio of rate constants.)

## Reaction Mechanisms

### Review Questions

- 14.39** What do we mean by the mechanism of a reaction?
- 14.40** What is an elementary step?
- 14.41** What is the molecularity of a reaction?
- 14.42** Reactions can be classified as unimolecular, bimolecular, and so on. Why are there no zero-molecular reactions?
- 14.43** Explain why termolecular reactions are rare.
- 14.44** What is the rate-determining step of a reaction? Give an everyday analogy to illustrate the meaning of the term “rate determining.”

- 14.45** The equation for the combustion of ethane ( $\text{C}_2\text{H}_6$ ) is

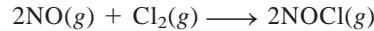


Explain why it is unlikely that this equation also represents the elementary step for the reaction.

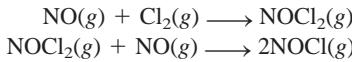
- 14.46** Which of these species cannot be isolated in a reaction: activated complex, product, intermediate?

### Problems

- 14.47** The rate law for the reaction



is given by  $\text{rate} = k[\text{NO}][\text{Cl}_2]$ . (a) What is the order of the reaction? (b) A mechanism involving these steps has been proposed for the reaction



If this mechanism is correct, what does it imply about the relative rates of these two steps?

- 14.48** For the reaction  $X_2 + Y + Z \longrightarrow XY + XZ$  it is found that doubling the concentration of  $X_2$  doubles the reaction rate, tripling the concentration of  $Y$  triples the rate, and doubling the concentration of  $Z$  has no effect. (a) What is the rate law for this reaction? (b) Why is it that the change in the concentration of  $Z$  has no effect on the rate? (c) Suggest a mechanism for the reaction that is consistent with the rate law.

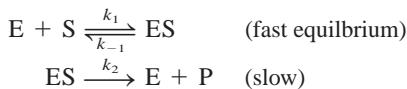
## Catalysis

### Review Questions

- 14.49 How does a catalyst increase the rate of a reaction?
- 14.50 What are the characteristics of a catalyst?
- 14.51 A certain reaction is known to proceed slowly at room temperature. Is it possible to make the reaction proceed at a faster rate without changing the temperature?
- 14.52 Distinguish between homogeneous catalysis and heterogeneous catalysis. Describe some important industrial processes that utilize heterogeneous catalysis.
- 14.53 Are enzyme-catalyzed reactions examples of homogeneous or heterogeneous catalysis?
- 14.54 The concentrations of enzymes in cells are usually quite small. What is the biological significance of this fact?

### Problems

- 14.55 Most reactions, including enzyme-catalyzed reactions, proceed faster at higher temperatures. However, for a given enzyme, the rate drops off abruptly at a certain temperature. Account for this behavior.
- 14.56** Consider this mechanism for the enzyme-catalyzed reaction



Derive an expression for the rate law of the reaction in terms of the concentrations of  $E$  and  $S$ . (*Hint:* To solve for  $[ES]$ , make use of the fact that, at equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction.)

### Additional Problems

- 14.57 Suggest experimental means by which the rates of the following reactions could be followed:
- $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$
  - $\text{Cl}_2(g) + 2\text{Br}^-(aq) \longrightarrow \text{Br}_2(aq) + 2\text{Cl}^-(aq)$
  - $\text{C}_2\text{H}_6(g) \longrightarrow \text{C}_2\text{H}_4(g) + \text{H}_2(g)$

- 14.58** List four factors that influence the rate of a reaction.

- 14.59 “The rate constant for the reaction



is  $1.64 \times 10^{-6}/M \cdot \text{s}$ .” What is incomplete about this statement?

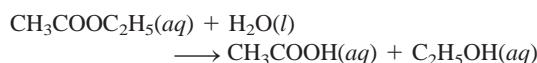
- 14.60** In a certain industrial process using a heterogeneous catalyst, the volume of the catalyst (in the shape of a sphere) is  $10.0 \text{ cm}^3$ . Calculate the surface area of the catalyst. If the sphere is broken down into eight spheres, each of which has a volume of  $1.25 \text{ cm}^3$ , what is the total surface area of the spheres? Which of the two geometric configurations of the catalyst is more effective? Explain. (The surface area of a sphere is  $4\pi r^2$ , in which  $r$  is the radius of the sphere.)

- 14.61 When methyl phosphate is heated in acid solution, it reacts with water:



If the reaction is carried out in water enriched with  $^{18}\text{O}$ , the oxygen-18 isotope is found in the phosphoric acid product but not in the methanol. What does this tell us about the bond-breaking scheme in the reaction?

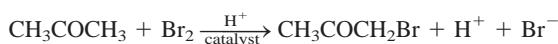
- 14.62** The rate of the reaction



shows first-order characteristics—that is, rate =  $k[\text{CH}_3\text{COOC}_2\text{H}_5]$ —even though this is a second-order reaction (first order in  $\text{CH}_3\text{COOC}_2\text{H}_5$  and first order in  $\text{H}_2\text{O}$ ). Explain.

- 14.63 Explain why most metals used in catalysis are transition metals.

- 14.64** The bromination of acetone is acid-catalyzed:



The rate of disappearance of bromine was measured for several different concentrations of acetone, bromine, and  $\text{H}^+$  ions at a certain temperature:

|     | Rate of Disappearance of $\text{Br}_2$ (M/s) |                 |                |                      |
|-----|--|-----------------|----------------|----------------------|
|     | $[\text{CH}_3\text{COCH}_3]$                 | $[\text{Br}_2]$ | $[\text{H}^+]$ |                      |
| (a) | 0.30   | 0.050           | 0.050          | $5.7 \times 10^{-5}$ |
| (b) | 0.30   | 0.10            | 0.050          | $5.7 \times 10^{-5}$ |
| (c) | 0.30   | 0.050           | 0.10           | $1.2 \times 10^{-4}$ |
| (d) | 0.40   | 0.050           | 0.20           | $3.1 \times 10^{-4}$ |
| (e) | 0.40   | 0.050           | 0.050          | $7.6 \times 10^{-5}$ |

(a) What is the rate law for the reaction? (b) Determine the rate constant.

- 14.65 The reaction  $2\text{A} + 3\text{B} \longrightarrow \text{C}$  is first order with respect to  $\text{A}$  and  $\text{B}$ . When the initial concentrations are

$[A] = 1.6 \times 10^{-2} M$  and  $[B] = 2.4 \times 10^{-3} M$ , the rate is  $4.1 \times 10^{-4} M/s$ . Calculate the rate constant of the reaction.

- 14.66** The decomposition of  $N_2O$  to  $N_2$  and  $O_2$  is a first-order reaction. At  $730^\circ C$  the half-life of the reaction is  $3.58 \times 10^3$  min. If the initial pressure of  $N_2O$  is 2.10 atm at  $730^\circ C$ , calculate the total gas pressure after one half-life. Assume that the volume remains constant.

- 14.67** The reaction  $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$  proceeds slowly in aqueous solution, but it can be catalyzed by the  $Fe^{3+}$  ion. Given that  $Fe^{3+}$  can oxidize  $I^-$  and  $Fe^{2+}$  can reduce  $S_2O_8^{2-}$ , write a plausible two-step mechanism for this reaction. Explain why the uncatalyzed reaction is slow.

- 14.68** What are the units of the rate constant for a third-order reaction?
- 14.69** Consider the zero-order reaction  $A \rightarrow B$ . Sketch the following plots: (a) rate versus  $[A]$  and (b)  $[A]$  versus  $t$ .

- 14.70** A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives are 50.0 min for A and 18.0 min for B. If the concentrations of A and B are equal initially, how long will it take for the concentration of A to be four times that of B?

- 14.71** Referring to the decomposition of  $N_2O_5$  in Problem 14.33, explain how you would measure the partial pressure of  $N_2O_5$  as a function of time.

- 14.72** The rate law for the reaction  $2NO_2(g) \rightarrow N_2O_4(g)$  is rate =  $k[NO_2]^2$ . Which of these changes will change the value of  $k$ ? (a) The pressure of  $NO_2$  is doubled. (b) The reaction is run in an organic solvent. (c) The volume of the container is doubled. (d) The temperature is decreased. (e) A catalyst is added to the container.

- 14.73** The reaction of  $G_2$  with  $E_2$  to form  $2EG$  is exothermic, and the reaction of  $G_2$  with  $X_2$  to form  $2XG$  is endothermic. The activation energy of the exothermic reaction is greater than that of the endothermic reaction. Sketch the potential energy profile diagrams for these two reactions on the same graph.

- 14.74** In the nuclear industry, workers use a rule of thumb that the radioactivity from any sample will be relatively harmless after 10 half-lives. Calculate the fraction of a radioactive sample that remains after this time. (*Hint:* Radioactive decays obey first-order kinetics.)

- 14.75** Briefly comment on the effect of a catalyst on each of the following: (a) activation energy, (b) reaction mechanism, (c) enthalpy of reaction, (d) rate of forward step, (e) rate of reverse step.

- 14.76** A quantity of 6 g of granulated Zn is added to a solution of 2 M HCl in a beaker at room temperature.

Hydrogen gas is generated. For each of the following changes (at constant volume of the acid) state whether the rate of hydrogen gas evolution will be increased, decreased, or unchanged: (a) 6 g of powdered Zn is used; (b) 4 g of granulated Zn is used; (c) 2 M acetic acid is used instead of 2 M HCl; (d) temperature is raised to  $40^\circ C$ .

- 14.77** These data were collected for the reaction between hydrogen and nitric oxide at  $700^\circ C$ :

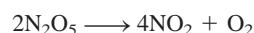


| Experiment | $[H_2]$ | $[NO]$ | Initial Rate (M/s)    |
|------------|---------|--------|-----------------------|
| 1          | 0.010   | 0.025  | $2.4 \times 10^{-6}$  |
| 2          | 0.0050  | 0.025  | $1.2 \times 10^{-6}$  |
| 3          | 0.010   | 0.0125 | $0.60 \times 10^{-6}$ |

(a) Determine the order of the reaction. (b) Calculate the rate constant. (c) Suggest a plausible mechanism that is consistent with the rate law. (*Hint:* Assume the oxygen atom is the intermediate.)

- 14.78** A certain first-order reaction is 35.5 percent complete in 4.90 min at  $25^\circ C$ . What is its rate constant?

- 14.79** The decomposition of dinitrogen pentoxide has been studied in carbon tetrachloride solvent ( $CCl_4$ ) at a certain temperature:



| $[N_2O_5]$ (M) | Initial Rate (M/s)    |
|----------------|-----------------------|
| 0.92           | $0.95 \times 10^{-5}$ |
| 1.23           | $1.20 \times 10^{-5}$ |
| 1.79           | $1.93 \times 10^{-5}$ |
| 2.00           | $2.10 \times 10^{-5}$ |
| 2.21           | $2.26 \times 10^{-5}$ |

Determine graphically the rate law for the reaction and calculate the rate constant.

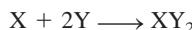
- 14.80** The thermal decomposition of  $N_2O_5$  obeys first-order kinetics. At  $45^\circ C$ , a plot of  $\ln [N_2O_5]$  versus  $t$  gives a slope of  $-6.18 \times 10^{-4} \text{ min}^{-1}$ . What is the half-life of the reaction?

- 14.81** When a mixture of methane and bromine is exposed to light, the following reaction occurs slowly:



Suggest a reasonable mechanism for this reaction. (*Hint:* Bromine vapor is deep red; methane is colorless.)

- 14.82** Consider this elementary step:



- (a) Write a rate law for this reaction. (b) If the initial rate of formation of  $XY_2$  is  $3.8 \times 10^{-3} M/s$  and the initial concentrations of X and Y are 0.26 M and 0.88 M, what is the rate constant of the reaction?

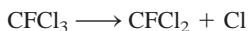
- 14.83 Consider the reaction



How could you follow the progress of the reaction by measuring the electrical conductance of the solution?

- 14.84** A compound X undergoes two *simultaneous* first-order reactions as follows:  $\text{X} \longrightarrow \text{Y}$  with rate constant  $k_1$  and  $\text{X} \longrightarrow \text{Z}$  with rate constant  $k_2$ . The ratio of  $k_1/k_2$  at  $40^\circ\text{C}$  is 8.0. What is the ratio at  $300^\circ\text{C}$ ? Assume that the frequency factor of the two reactions is the same.

- 14.85 In recent years ozone in the stratosphere has been depleted at an alarmingly fast rate by chlorofluorocarbons (CFCs). A CFC molecule such as  $\text{CFCl}_3$  is first decomposed by UV radiation:



The chlorine radical then reacts with ozone as follows:

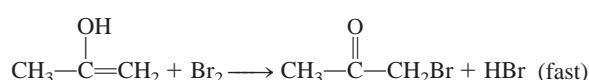
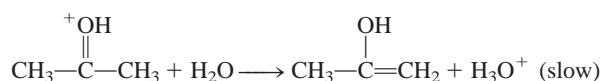
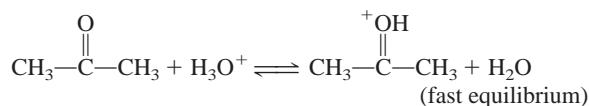


(a) Write the overall reaction for the last two steps. (b) What are the roles of Cl and ClO? (c) Why is the fluorine radical not important in this mechanism? (d) One suggestion to reduce the concentration of chlorine radicals is to add hydrocarbons such as ethane ( $\text{C}_2\text{H}_6$ ) to the stratosphere. How will this work?

- 14.86** Consider a car fitted with a catalytic converter. The first 10 min or so after it is started are the most polluting. Why?

- 14.87 Strontium-90, a radioactive isotope, is a major product of an atomic bomb explosion. It has a half-life of 28.1 yr. (a) Calculate the first-order rate constant for the nuclear decay. (b) Calculate the fraction of  ${}^{90}\text{Sr}$  that remains after 10 half-lives. (c) Calculate the number of years required for 99.0 percent of  ${}^{90}\text{Sr}$  to disappear.

- 14.88** The following mechanism has been proposed for the reaction described in Problem 14.64:



Show that the rate law deduced from the mechanism is consistent with that shown in (a) of Problem 14.64.

- 14.89 The integrated rate law for the zero-order reaction  $\text{A} \longrightarrow \text{B}$  is  $[A]_t = [A]_0 - kt$ . (a) Sketch the following plots: (i) rate versus  $[A]_t$ , and (ii)  $[A]_t$  versus  $t$ . (b) Derive an expression for the half-life of the reaction. (c) Calculate the time in half-lives when the integrated rate law is no longer valid, that is, when  $[A]_t = 0$ .

- 14.90** Strictly speaking, the rate law derived for the reaction in Problem 14.77 applies only to certain concentrations of  $\text{H}_2$ . The general rate law for the reaction takes the form

$$\text{rate} = \frac{k_1[\text{NO}]^2[\text{H}_2]}{1 + k_2[\text{H}_2]}$$

in which  $k_1$  and  $k_2$  are constants. Derive rate law expressions under the conditions of very high and very low hydrogen concentrations. Does the result from Problem 14.77 agree with one of the rate expressions here?

- 14.91 (a) What can you deduce about the activation energy of a reaction if its rate constant changes significantly with a small change in temperature? (b) If a bimolecular reaction occurs every time an A and a B molecule collide, what can you say about the orientation factor and activation energy of the reaction?

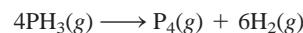
- 14.92** The rate law for this reaction



is  $\text{rate} = k[\text{NO}_2]^2$ . Suggest a plausible mechanism for the reaction, given that the unstable species  $\text{NO}_3$  is an intermediate.

- 14.93 Radioactive plutonium-239 ( $t_{1/2} = 2.44 \times 10^5$  yr) is used in nuclear reactors and atomic bombs. If there are  $5.0 \times 10^2$  g of the isotope in a small atomic bomb, how long will it take for the substance to decay to  $1.0 \times 10^2$  g, too small an amount for an effective bomb? (Hint: Radioactive decays follow first-order kinetics.)

- 14.94** Many reactions involving heterogeneous catalysts are zero order; that is,  $\text{rate} = k$ . An example is the decomposition of phosphine ( $\text{PH}_3$ ) over tungsten (W):

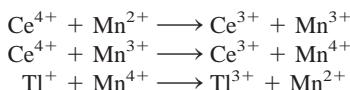


It is found that the reaction is independent of  $[\text{PH}_3]$  as long as phosphine's pressure is sufficiently high ( $\geq 1$  atm). Explain.

- 14.95 Thallium(I) is oxidized by cerium(IV) as follows:



The elementary steps, in the presence of Mn(II), are as follows:



(a) Identify the catalyst, intermediates, and the rate-determining step if the rate law is given by rate =  $k[\text{Ce}^{4+}][\text{Mn}^{2+}]$ . (b) Explain why the reaction is slow without the catalyst. (c) Classify the type of catalysis (homogeneous or heterogeneous).

- 14.96** Consider the following elementary steps for a consecutive reaction:

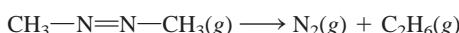


- (a) Write an expression for the rate of change of B.  
 (b) Derive an expression for the concentration of B under steady-state conditions; that is, when B is decomposing to C at the same rate as it is formed from A.

- 14.97 For gas-phase reactions, we can replace the concentration terms in Equation (14.3) with the pressures of the gaseous reactant. (a) Derive the equation

$$\ln \frac{P_t}{P_0} = -kt$$

where  $P_i$  and  $P_0$  are the pressures at  $t = t$  and  $t = 0$ , respectively. (b) Consider the decomposition of azomethane.

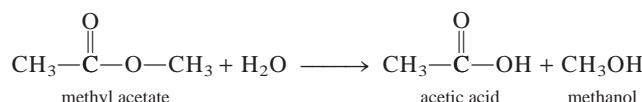


The data obtained at 300°C are shown in the following table:

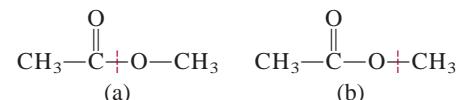
| Time (s) | Partial Pressure of Azomethane (mmHg) |
|----------|---------------------------------------|
| 0        | 284                                   |
| 100      | 220                                   |
| 150      | 193                                   |
| 200      | 170                                   |
| 250      | 150                                   |
| 300      | 132                                   |

Are these values consistent with first-order kinetics? If so, determine the rate constant by plotting the data as shown in Figure 14.7(b). (c) Determine the rate constant by the half-life method.

**14.98** The hydrolysis of methyl acetate

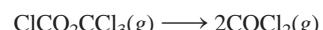


involves the breaking of a C—O bond. The two possibilities are



Suggest an experiment that would enable you to distinguish between these two possibilities.

- 14.99 The following gas-phase reaction was studied at 290°C by observing the change in pressure as a function of time in a constant-volume vessel:

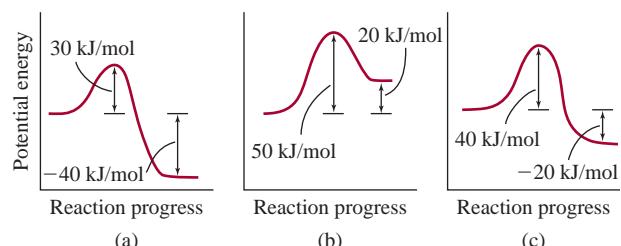


Determine the order of the reaction and the rate constant based on the following data:

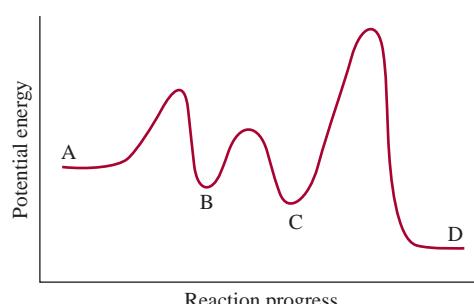
| Time (s) | P (mmHg) |
|----------|----------|
| 0        | 15.76    |
| 181      | 18.88    |
| 513      | 22.79    |
| 1164     | 27.08    |

where  $P$  is the total pressure

- 14.100** Consider the potential energy profiles for the following three reactions (from left to right). (1) Rank the rates (slowest to fastest) of the reactions. (2) Calculate  $\Delta H$  for each reaction and determine which reaction(s) are exothermic and which reaction(s) are endothermic. Assume the reactions have roughly the same frequency factors.

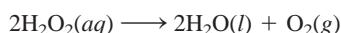


- 14.101 Consider the following potential energy profile for the A  $\longrightarrow$  D reaction. (a) How many elementary steps are there? (b) How many intermediates are formed? (c) Which step is rate determining? (d) Is the overall reaction exothermic or endothermic?



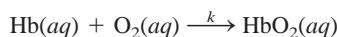
**14.102** A factory that specializes in the refinement of transition metals such as titanium was on fire. The fire-fighters were advised not to douse the fire with water. Why?

**14.103** The activation energy for the decomposition of hydrogen peroxide



is 42 kJ/mol, whereas when the reaction is catalyzed by the enzyme catalase, it is 7.0 kJ/mol. Calculate the temperature that would cause the nonenzymatic catalysis to proceed as rapidly as the enzymecatalyzed decomposition at 20°C. Assume the frequency factor A to be the same in both cases.

**14.104** To carry out metabolism, oxygen is taken up by hemoglobin (Hb) to form oxyhemoglobin ( $\text{HbO}_2$ ) according to the simplified equation

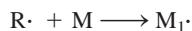


## SPECIAL PROBLEMS

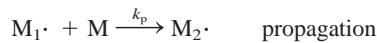
**14.105** Polyethylene is used in many items such as water pipes, bottles, electrical insulation, toys, and mailer envelopes. It is a *polymer*, a molecule with a very high molar mass made by joining many ethylene molecules (the basic unit is called a monomer) together (see p. 369). The initiation step is



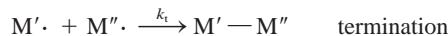
The  $\text{R} \cdot$  species (called a radical) reacts with an ethylene molecule (M) to generate another radical



Reaction of  $\text{M}_1 \cdot$  with another monomer leads to the growth or propagation of the polymer chain:



This step can be repeated with hundreds of monomer units. The propagation terminates when two radicals combine



(a) The initiator used in the polymerization of ethylene is benzoyl peroxide  $[(\text{C}_6\text{H}_5\text{COO})_2]$ :



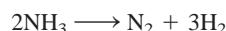
This is a first-order reaction. The half-life of benzoyl peroxide at 100°C is 19.8 min. (a) Calculate the rate constant (in  $\text{min}^{-1}$ ) of the reaction. (b) If the half-

where the second-order rate constant is  $2.1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$  at 37°C. (The reaction is first order in Hb and  $\text{O}_2$ .) For an average adult, the concentrations of Hb and  $\text{O}_2$  in the blood at the lungs are  $8.0 \times 10^{-6} \text{ M}$  and  $1.5 \times 10^{-6} \text{ M}$ , respectively. (a) Calculate the rate of formation of  $\text{HbO}_2$ . (b) Calculate the rate of consumption of  $\text{O}_2$ . (c) The rate of formation of  $\text{HbO}_2$  increases to  $1.4 \times 10^{-4} \text{ M/s}$  during exercise to meet the demand of increased metabolism rate. Assuming the Hb concentration to remain the same, what must be the oxygen concentration to sustain this rate of  $\text{HbO}_2$  formation?

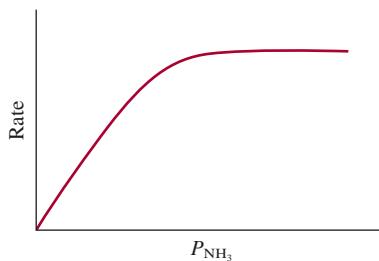
life of benzoyl peroxide is 7.30 h or 438 min, at 70°C, what is the activation energy (in kJ/mol) for the decomposition of benzoyl peroxide? (c) Write the rate laws for the elementary steps in the above polymerization process and identify the reactant, product, and intermediates. (d) What condition would favor the growth of long high-molar-mass polyethylenes?

**14.106** Ethanol is a toxic substance that, when consumed in excess, can impair respiratory and cardiac functions by interference with the neurotransmitters of the nervous system. In the human body, ethanol is metabolized by the enzyme alcohol dehydrogenase to acetaldehyde, which causes “hangovers.” (a) Based on your knowledge of enzyme kinetics, explain why binge drinking (that is, consuming too much alcohol too fast) can prove fatal. (b) Methanol is even more toxic than ethanol. It is also metabolized by alcohol dehydrogenase, and the product, formaldehyde, can cause blindness or death. An antidote to methanol poisoning is ethanol. Explain how this procedure works.

**14.107** At a certain elevated temperature, ammonia decomposes on the surface of tungsten metal as follows:



From the following plot of the rate of the reaction versus the pressure of  $\text{NH}_3$ , describe the mechanism of the reaction.

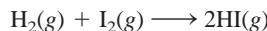


- 14.108** The following expression shows the dependence of the half-life of a reaction ( $t_{\frac{1}{2}}$ ) on the initial reactant concentration  $[A]_0$ :

$$t_{\frac{1}{2}} \propto \frac{1}{[A]_0^{n-1}}$$

where  $n$  is the order of the reaction. Verify this dependence for zero-, first-, and second-order reactions.

- 14.109** The rate constant for the gaseous reaction

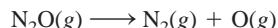


is  $2.42 \times 10^{-2} M \cdot \text{s}$  at  $400^\circ\text{C}$ . Initially an equimolar sample of  $\text{H}_2$  and  $\text{I}_2$  is placed in a vessel at  $400^\circ\text{C}$  and the total pressure is 1658 mmHg. (a) What is the initial rate ( $M/\text{min}$ ) of formation of  $\text{HI}$ ? (b) What are the rate of formation of  $\text{HI}$  and the concentration of  $\text{HI}$  (in molarity) after 10.0 min?

- 14.110** When the concentration of A in the reaction  $\text{A} \longrightarrow \text{B}$  was changed from  $1.20 M$  to  $0.60 M$ , the

half-life increased from 2.0 min to 4.0 min at  $25^\circ\text{C}$ . Calculate the order of the reaction and the rate constant. (Hint: Use the equation in Problem 14.108.)

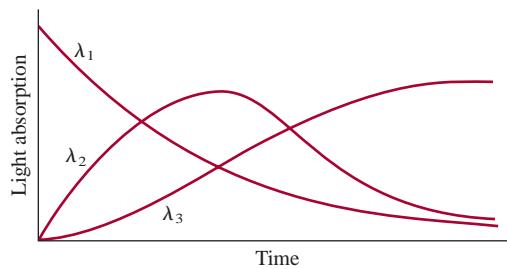
- 14.111** The activation energy for the reaction



is  $2.4 \times 10^2 \text{ kJ/mol}$  at  $600 \text{ K}$ . Calculate the percentage of the increase in rate from  $600 \text{ K}$  to  $606 \text{ K}$ . Comment on your results.

- 14.112** The rate of a reaction was followed by the absorption of light by the reactants and products as a function of wavelengths ( $\lambda_1, \lambda_2, \lambda_3$ ) as time progresses. Which of the following mechanisms is consistent with the experimental data?

- (a)  $\text{A} \longrightarrow \text{B}, \text{A} \longrightarrow \text{C}$
- (b)  $\text{A} \longrightarrow \text{B} + \text{C}$
- (c)  $\text{A} \longrightarrow \text{B}, \text{B} \longrightarrow \text{C} + \text{D}$
- (d)  $\text{A} \longrightarrow \text{B}, \text{B} \longrightarrow \text{C}$



## ANSWERS TO PRACTICE EXERCISES

**14.1** rate =  $-\frac{\Delta[\text{CH}_4]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{CO}_2]}{\Delta t} =$

$\frac{1}{2} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$ . **14.2** (a)  $0.013 M/\text{s}$ , (b)  $-0.052 M/\text{s}$ .

**14.3** rate =  $k[\text{S}_2\text{O}_8^{2-}][\text{I}^-]$ ;  $k = 8.1 \times 10^{-2} M \cdot \text{s}$ .

**14.4** 66 s. **14.5**  $1.2 \times 10^3 \text{ s}$ . **14.6** (a) 3.2 min, (b) 2.1 min.

**14.7** 240 kJ/mol. **14.8**  $3.13 \times 10^{-9} \text{ s}^{-1}$ .

**14.9** (a)  $\text{NO}_2 + \text{CO} \longrightarrow \text{NO} + \text{CO}_2$ , (b)  $\text{NO}_3$ , (c) the first step is rate-determining.



The equilibrium between  $\text{N}_2\text{O}_4$  (colorless) and  $\text{NO}_2$  (brown in color) gases favors the formation of the latter as temperature increases (from bottom to top.)

## Chemical Equilibrium

### CHAPTER OUTLINE

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The Equilibrium Constant

#### 15.2 Ways of Expressing Equilibrium Constants 500

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#### 15.3 What Does the Equilibrium Constant Tell Us? 507

Predicting the Direction of a Reaction • Calculating Equilibrium Concentrations

#### 15.4 Factors That Affect Chemical Equilibrium 512

Le Châtelier's Principle • Changes in Concentrations • Changes in Pressure and Volume • Changes in Temperature • The Effect of a Catalyst • Summary of Factors That May Affect the Equilibrium Position

### ESSENTIAL CONCEPTS

**Chemical Equilibrium** Chemical Equilibrium describes the state in which the rates of forward and reverse reactions are equal and the concentrations of the reactants and products remain unchanged with time. This state of dynamic equilibrium is characterized by an equilibrium constant. Depending on the nature of reacting species, the equilibrium constant can be expressed in terms of molarities (for solutions) or partial pressures (for gases). The Equilibrium constant provides information about the net direction of a reversible reaction and the concentrations of the equilibrium mixture.

**Factors That Affect Chemical Equilibrium** Changes in concentration can affect the position of an equilibrium state—that is, the relative amounts of reactants and products. Changes in pressure and volume may have the same effect for gaseous systems at equilibrium. Only a change in temperature can alter the value of equilibrium constant. A catalyst can establish the equilibrium state faster by speeding the forward and reverse reactions, but it can change neither the equilibrium position nor the equilibrium constant.

### Interactive



### Activity Summary

1. Animation: Chemical Equilibrium (15.1)
2. Interactivity: Determining Extent—Equilibrium Constant (15.3)
3. Interactivity: Determining Extent—Concentration from Equilibrium Expression (15.3)
4. Animation: Le Châtelier's Principle (15.4)

## 15.1 The Concept of Equilibrium

Few chemical reactions proceed in only one direction. Most are, at least to some extent, reversible. At the start of a reversible process, the reaction proceeds toward the formation of products. As soon as some product molecules are formed, the reverse process—that is, the formation of reactant molecules from product molecules—begins to take place. *When the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products no longer change with time, chemical equilibrium is reached.*

Chemical equilibrium is a dynamic process. As such, it can be likened to the movement of skiers at a busy ski resort, where the number of skiers carried up the mountain on the chair lift is equal to the number coming down the slopes. Thus, although there is a constant transfer of skiers, the number of people at the top and the number at the bottom of the slope do not change.

Note that a chemical equilibrium reaction involves different substances as reactants and products. Equilibrium between two phases of the same substance is called **physical equilibrium** because *the changes that occur are physical processes*. The vaporization of water in a closed container at a given temperature is an example of physical equilibrium. In this instance, the number of H<sub>2</sub>O molecules leaving and the number returning to the liquid phase are equal:



(Recall from Chapter 4 that the double arrow means that the reaction is reversible.) The study of physical equilibrium yields useful information, such as the equilibrium vapor pressure (see Section 12.6). However, chemists are particularly interested in chemical equilibrium processes, such as the reversible reaction involving nitrogen dioxide (NO<sub>2</sub>) and dinitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>). The progress of the reaction



can be monitored easily because N<sub>2</sub>O<sub>4</sub> is a colorless gas, whereas NO<sub>2</sub> has a dark-brown color that makes it sometimes visible in polluted air. Suppose that a known amount of N<sub>2</sub>O<sub>4</sub> is injected into an evacuated flask. Some brown color appears immediately, indicating the formation of NO<sub>2</sub> molecules. The color intensifies as the dissociation of N<sub>2</sub>O<sub>4</sub> continues until eventually equilibrium is reached. Beyond that point, no further change in color is observed. By experiment we find that we can also reach the equilibrium state by starting with pure NO<sub>2</sub> or with a mixture of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub>. In each case, we observe an initial change in color, caused either by the formation of NO<sub>2</sub> (if the color intensifies) or by the depletion of NO<sub>2</sub> (if the color fades), and then the final state in which the color of NO<sub>2</sub> no longer changes. Depending on the temperature of the reacting system and on the initial amounts of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub>, the concentrations of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> at equilibrium differ from system to system (Figure 15.1).

### The Equilibrium Constant

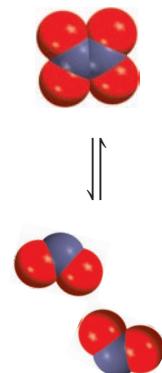
Table 15.1 shows some experimental data for this reaction at 25°C. The gas concentrations are expressed in molarity, which can be calculated from the number of moles of gases present initially and at equilibrium and the volume of the flask in liters. Note that the equilibrium concentrations of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> vary, depending on the starting concentrations. We can look for relationships between [NO<sub>2</sub>] and [N<sub>2</sub>O<sub>4</sub>] present at equilibrium by comparing the ratios of their concentrations. The simplest ratio, that



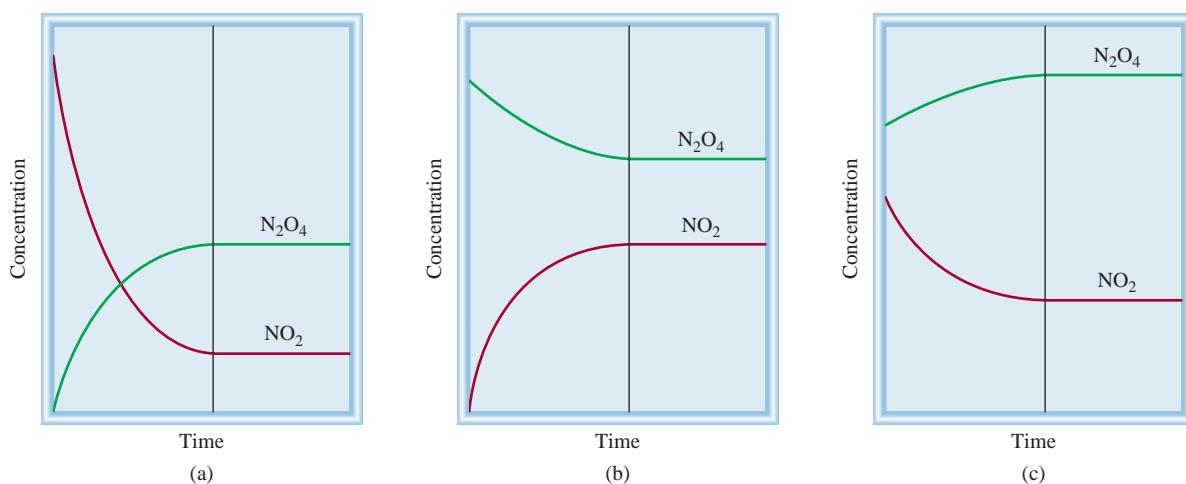
**Animation:**  
Chemical Equilibrium  
ARIS Animations



Liquid water in equilibrium with its vapor in a closed system at room temperature.



NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> gases at equilibrium.

**Figure 15.1**

Change in the concentrations of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  with time, in three situations. (a) Initially only  $\text{NO}_2$  is present. (b) Initially only  $\text{N}_2\text{O}_4$  is present. (c) Initially a mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  is present. In each case, equilibrium is established to the right of the vertical line.

is,  $[\text{NO}_2]/[\text{N}_2\text{O}_4]$ , gives scattered values. But if we examine other possible mathematical relationships, we find that the ratio  $[\text{NO}_2]^2/[\text{N}_2\text{O}_4]$  at equilibrium gives a nearly constant value that averages  $4.63 \times 10^{-3}$ , regardless of the initial concentrations present:

$$K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 4.63 \times 10^{-3} \quad (15.1)$$

Note that the exponent 2 in  $[\text{NO}_2]^2$  is the same as the stoichiometric coefficient for  $\text{NO}_2$  in the reversible equation. It turns out that for every reversible reaction, there is a specific mathematical ratio between the equilibrium concentrations of products and reactants that yields a constant value.

We can generalize this discussion by considering the following reversible reaction:

**TABLE 15.1** The  $\text{NO}_2$ - $\text{N}_2\text{O}_4$  System at 25° C

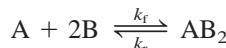
| Initial Concentrations (M) |                                  | Equilibrium Concentrations (M) |                                  | Ratio of Concentrations at Equilibrium              |  |
|----------------------------|----------------------------------|--------------------------------|----------------------------------|---|--|
| [NO <sub>2</sub> ]         | [N <sub>2</sub> O <sub>4</sub> ] | [NO <sub>2</sub> ]             | [N <sub>2</sub> O <sub>4</sub> ] | [NO <sub>2</sub> ]/[N <sub>2</sub> O <sub>4</sub> ] | [NO <sub>2</sub> <sup>2</sup> ]/[N <sub>2</sub> O <sub>4</sub> ] |
| 0.000                      | 0.670                            | 0.0547                         | 0.643                            | 0.0851  | $4.65 \times 10^{-3}$  |
| 0.0500                     | 0.446                            | 0.0457                         | 0.448                            | 0.102   | $4.66 \times 10^{-3}$  |
| 0.0300                     | 0.500                            | 0.0475                         | 0.491                            | 0.0967  | $4.60 \times 10^{-3}$  |
| 0.0400                     | 0.600                            | 0.0523                         | 0.594                            | 0.0880  | $4.60 \times 10^{-3}$  |
| 0.200                      | 0.000                            | 0.0204                         | 0.0898                           | 0.227   | $4.63 \times 10^{-3}$  |

in which  $a$ ,  $b$ ,  $c$ , and  $d$  are the stoichiometric coefficients for the reacting species A, B, C, and D. The equilibrium constant for the reaction at a particular temperature is

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (15.2)$$

Equation (15.2) is the mathematical form of the *law of mass action*. It relates the concentrations of reactants and products at equilibrium in terms of a quantity called the **equilibrium constant**. The equilibrium constant is defined by a quotient. The numerator is obtained by multiplying together the equilibrium concentrations of the products, each raised to a power equal to its stoichiometric coefficient in the balanced equation. The same procedure is applied to the equilibrium concentrations of *reactants* to obtain the denominator. This formulation is based on purely empirical evidence, such as the study of reactions like  $\text{NO}_2\text{-N}_2\text{O}_4$ .

The equilibrium constant has its origin in thermodynamics, to be discussed in Chapter 18. However, we can gain some insight into  $K$  by considering the kinetics of chemical reactions. Let us suppose that this reversible reaction occurs via a mechanism of a single *elementary step* in both the forward and reverse directions:



The forward rate is given by

$$\text{rate}_f = k_f[\text{A}][\text{B}]^2$$

and the reverse rate is

$$\text{rate}_r = k_r[\text{AB}_2]$$

in which  $k_f$  and  $k_r$  are the rate constants for the forward and reverse directions, respectively. At equilibrium, when no net changes occur, the two rates must be equal:

$$\text{rate}_f = \text{rate}_r$$

or

$$\begin{aligned} k_f[\text{A}][\text{B}]^2 &= k_r[\text{AB}_2] \\ \frac{k_f}{k_r} &= \frac{[\text{AB}_2]}{[\text{A}][\text{B}]^2} \end{aligned}$$

Because both  $k_f$  and  $k_r$  are constants at a given temperature, their ratio is also a constant, which is equal to the equilibrium constant  $K_c$ .

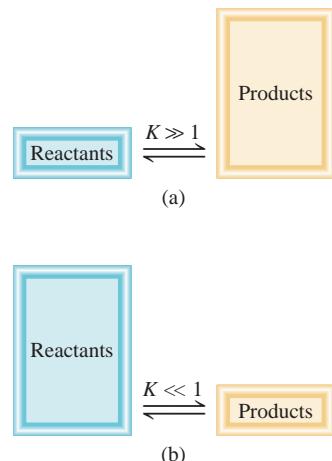
$$\frac{k_f}{k_r} = K_c = \frac{[\text{AB}_2]}{[\text{A}][\text{B}]^2}$$

So  $K_c$  is a constant regardless of the equilibrium concentrations of the reacting species because it is always equal to  $k_f/k_r$ , the quotient of two quantities that are themselves constant at a given temperature. Because rate constants are temperature-dependent [see Equation (14.9)], it follows that the equilibrium constant must also change with temperature.

Finally, we note that if the equilibrium constant is much greater than 1 (that is,  $K \gg 1$ ), the equilibrium will lie to the right of the reaction arrows and favor the products. Conversely, if the equilibrium constant is much smaller than 1 (that is,  $K \ll 1$ ), the equilibrium will lie to the left and favor the reactants (Figure 15.2).

In keeping with the convention, we refer to substances on the left of the equilibrium arrows as "reactants" and those on the right as "products."

To review reaction mechanism, see Section 14.5.



**Figure 15.2**

(a) At equilibrium, there are more products than reactants, and the equilibrium is said to lie to the right. (b) In the opposite situation, when there are more reactants than products, the equilibrium is said to lie to the left.

The signs  $\gg$  and  $\ll$  signs mean "much greater than" and "much smaller than," respectively.

## 15.2 Ways of Expressing Equilibrium Constants

To use equilibrium constants, we must express them in terms of the reactant and product concentrations. Our only guidance is the law of mass action [Equation (15.2)]. However, because the concentrations of the reactants and products can be expressed in different units and because the reacting species are not always in the same phase, there may be more than one way to express the equilibrium constant for the *same* reaction. To begin with, we will consider reactions in which the reactants and products are in the same phase.

### Homogeneous Equilibria

The term ***homogeneous equilibrium*** applies to reactions in which *all reacting species are in the same phase*. An example of homogeneous gas-phase equilibrium is the dissociation of N<sub>2</sub>O<sub>4</sub>. The equilibrium constant, as given in Equation (15.1), is

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

Note that the subscript in  $K_c$  denotes that the concentrations of the reacting species are expressed in moles per liter. The concentrations of reactants and products in gaseous reactions can also be expressed in terms of their partial pressures. From Equation (5.8) we see that at constant temperature the pressure  $P$  of a gas is directly related to the concentration in moles per liter of the gas; that is,  $P = (n/V)RT$ . Thus, for the equilibrium process



we can write

$$K_P = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} \quad (15.3)$$

in which  $P_{\text{NO}_2}$  and  $P_{\text{N}_2\text{O}_4}$  are the equilibrium partial pressures (in atmospheres) of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub>, respectively. The subscript in  $K_P$  tells us that equilibrium concentrations are expressed in terms of pressure.

In general,  $K_c$  is not equal to  $K_P$ , because the partial pressures of reactants and products are not equal to their concentrations expressed in moles per liter. A simple relationship between  $K_P$  and  $K_c$  can be derived as follows. Let us consider this equilibrium in the gas phase:



in which  $a$  and  $b$  are stoichiometric coefficients. The equilibrium constant  $K_c$  is

$$K_c = \frac{[\text{B}]^b}{[\text{A}]^a}$$

and the expression for  $K_P$  is

$$K_P = \frac{P_{\text{B}}^b}{P_{\text{A}}^a}$$

in which  $P_{\text{A}}$  and  $P_{\text{B}}$  are the partial pressures of A and B. Assuming ideal gas behavior,

$$P_A V = n_A RT$$

$$P_A = \frac{n_A RT}{V}$$

in which  $V$  is the volume of the container in liters. Also,

$$P_B V = n_B RT$$

$$P_B = \frac{n_B RT}{V}$$

Substituting these relations into the expression for  $K_P$ , we obtain

$$K_P = \frac{\left(\frac{n_B RT}{V}\right)^b}{\left(\frac{n_A RT}{V}\right)^a} = \frac{\left(\frac{n_B}{V}\right)^b}{\left(\frac{n_A}{V}\right)^a} (RT)^{b-a}$$

Now both  $n_A/V$  and  $n_B/V$  have the units of moles per liter and can be replaced by  $[A]$  and  $[B]$ , so that

$$K_P = \frac{[B]^b}{[A]^a} (RT)^{\Delta n}$$

$$= K_c (RT)^{\Delta n} \quad (15.4)$$

in which

$$\begin{aligned} \Delta n &= b - a \\ &= \text{moles of gaseous products} - \text{moles of gaseous reactants} \end{aligned}$$

Because pressure is usually expressed in atmospheres, the gas constant  $R$  is given by 0.0821 L · atm/K · mol, and we can write the relationship between  $K_P$  and  $K_c$  as

$$K_P = K_c (0.0821T)^{\Delta n} \quad (15.5)$$

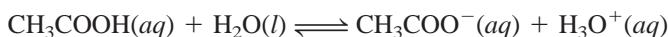
To use this equation, the pressures in  $K_P$  must be in atm.

In general,  $K_P \neq K_c$  except in the special case when  $\Delta n = 0$ . In that case, Equation (15.5) can be written as

$$\begin{aligned} K_P &= K_c (0.0821T)^0 \\ &= K_c \end{aligned}$$

Any number raised to the zero power is equal to 1.

As another example of homogeneous equilibrium, let us consider the ionization of acetic acid ( $\text{CH}_3\text{COOH}$ ) in water:



The equilibrium constant is

$$K'_c = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]}$$

(We use the prime for  $K_c$  here to distinguish it from the final form of equilibrium constant to be derived shortly.) However, in 1 L, or 1000 g, of water, there are

1000 g/(18.02 g/mol), or 55.5 mol, of water. Therefore, the “concentration” of water, or  $[H_2O]$ , is 55.5 mol/L, or 55.5 M. This is a large quantity compared with the concentrations of other species in solution (usually 1 M or smaller), and we can assume that it does not change appreciably during the course of a reaction. Thus, we can treat  $[H_2O]$  as a constant and rewrite the equilibrium constant as

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

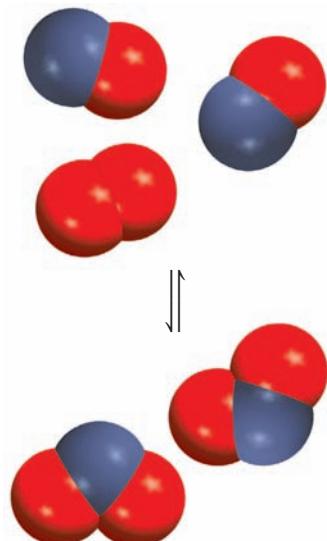
in which

$$K_c = K'_c[H_2O]$$

## Equilibrium Constant and Units

**For nonideal systems, the activities are not exactly numerically equal to concentrations. In some cases, the differences can be appreciable. Unless otherwise noted, we will treat all systems as ideal.**

Note that it is general practice not to include units for the equilibrium constant. In thermodynamics, the equilibrium constant is defined in terms of *activities* rather than concentrations. For an ideal system, the activity of a substance is the ratio of its concentration (or partial pressure) to a standard value, which is 1 M (or 1 atm). This procedure eliminates all units but does not alter the numerical parts of the concentration or pressure. Consequently,  $K$  has no units. We will extend this practice to acid-base equilibria and solubility equilibria in Chapters 16 and 17.



Reaction shown in (b).

### Example 15.1

Write expressions for  $K_c$ , and  $K_P$  if applicable, for the following reversible reactions at equilibrium:

- $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$
- $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$
- $CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(l)$

**Strategy** Keep in mind the following facts: (1) the  $K_P$  expression applies only to gaseous reactions and (2) the concentration of solvent (usually water) does not appear in the equilibrium constant expression.

**Solution** (a) Because there are no gases present,  $K_P$  does not apply and we have only  $K_c$ .

$$K'_c = \frac{[H_3O^+][F^-]}{[HF][H_2O]}$$

HF is a weak acid, so that the amount of water consumed in acid ionizations is negligible compared with the total amount of water present as solvent. Thus, we can rewrite the equilibrium constant as

$$K_c = \frac{[H_3O^+][F^-]}{[HF]}$$

(b)

$$K_c = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

$$K_P = \frac{P_{NO_2}^2}{P_{NO}^2 P_{O_2}}$$

(Continued)

(c) The equilibrium constant  $K'_c$  is given by

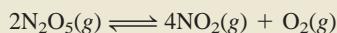
$$K'_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

Because the water produced in the reaction is negligible compared with the water solvent, the concentration of water does not change. Thus, we can write the new equilibrium constant as

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

**Similar problem:** 15.8.

**Practice Exercise** Write  $K_c$  and  $K_P$  for the decomposition of nitrogen pentoxide:



### Example 15.2

The equilibrium constant  $K_P$  for the decomposition of phosphorus pentachloride to phosphorus trichloride and molecular chlorine



is found to be 1.05 at 250°C. If the equilibrium partial pressures of  $\text{PCl}_5$  and  $\text{PCl}_3$  are 0.875 atm and 0.463 atm, respectively, what is the equilibrium partial pressure of  $\text{Cl}_2$  at 250°C?

**Strategy** The concentrations of the reacting gases are given in atm, so we can express the equilibrium constant in  $K_P$ . From the known  $K_P$  value and the equilibrium pressures of  $\text{PCl}_3$  and  $\text{PCl}_5$ , we can solve for  $P_{\text{Cl}_2}$ .

**Solution** First, we write  $K_P$  in terms of the partial pressures of the reacting species

$$K_P = \frac{P_{\text{PCl}_3} P_{\text{Cl}_2}}{P_{\text{PCl}_5}}$$

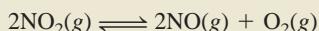
Knowing the partial pressures, we write

$$1.05 = \frac{(0.463)(P_{\text{Cl}_2})}{(0.875)}$$

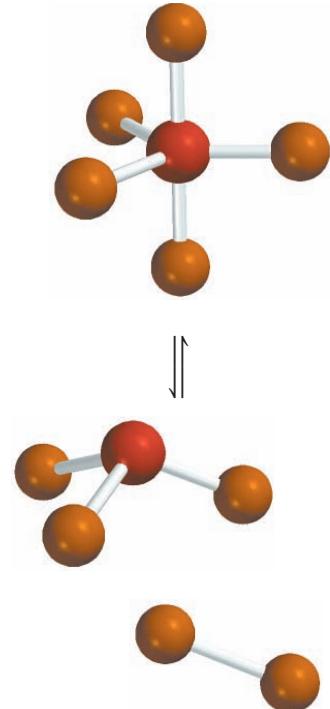
or  $P_{\text{Cl}_2} = \frac{(1.05)(0.875)}{(0.463)} = 1.98 \text{ atm}$

**Check** Note that we have added atm as the unit for  $P_{\text{Cl}_2}$ .

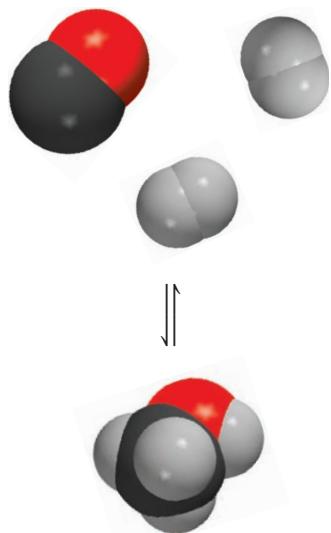
**Practice Exercise** The equilibrium constant  $K_P$  for the reaction



is 158 at 1000 K. Calculate  $P_{\text{O}_2}$  if  $P_{\text{NO}_2} = 0.400 \text{ atm}$  and  $P_{\text{NO}} = 0.270 \text{ atm}$ .

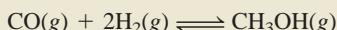


**Similar problem:** 15.17.



### Example 15.3

Methanol ( $\text{CH}_3\text{OH}$ ) is manufactured industrially by the reaction



The equilibrium constant ( $K_c$ ) for the reaction is 10.5 at  $220^\circ\text{C}$ . What is the value of  $K_P$  at this temperature?

**Strategy** The relationship between  $K_c$  and  $K_P$  is given by Equation (15.5). What is the change in the number of moles of gases from reactants to product? Recall that

$$\Delta n = \text{moles of gaseous products} - \text{moles of gaseous reactants}$$

What unit of temperature should we use?

**Solution** The relationship between  $K_c$  and  $K_P$  is

$$K_P = K_c(0.0821T)^{\Delta n}$$

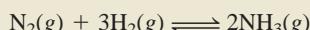
Because  $T = 273 + 220 = 493$  K and  $\Delta n = 1 - 3 = -2$ , we have

$$\begin{aligned} K_P &= (10.5)(0.0821 \times 493)^{-2} \\ &= 6.41 \times 10^{-3} \end{aligned}$$

**Check** Note that  $K_P$ , like  $K_c$ , is a dimensionless quantity. This example shows that we can get a quite different value for the equilibrium constant for the same reaction, depending on whether we express the concentrations in moles per liter or in atmospheres.

**Similar problem:** 15.15.

**Practice Exercise** For the reaction



$K_P$  is  $4.3 \times 10^{-4}$  at  $375^\circ\text{C}$ . Calculate  $K_c$  for the reaction.

## Heterogeneous Equilibria



The mineral calcite is made of calcium carbonate, as are chalk and marble.

A reversible reaction involving reactants and products that are in different phases leads to a **heterogeneous equilibrium**. For example, when calcium carbonate is heated in a closed vessel, this equilibrium is attained:

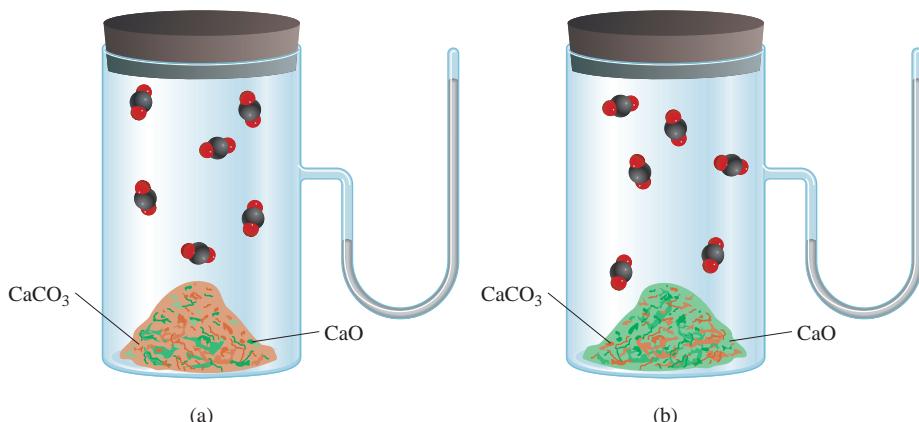


The two solids and one gas constitute three separate phases. At equilibrium, we might write the equilibrium constant as

$$K'_c = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]} \quad (15.6)$$

However, the “concentration” of a solid, like its density, is an intensive property and does not depend on how much of the substance is present. [Note that the units of concentration (moles per liter) can be converted to units of density (grams per cubic centimeters) and vice versa.] For this reason, the terms  $[\text{CaCO}_3]$  and  $[\text{CaO}]$  are themselves constants and can be combined with the equilibrium constant. We can simplify the equilibrium expression by writing

$$\frac{[\text{CaCO}_3]}{[\text{CaO}]} K'_c = K_c = [\text{CO}_2] \quad (15.7)$$



**Figure 15.3**  
*In (a) and (b) the equilibrium pressure of CO<sub>2</sub> is the same at the same temperature, despite the presence of different amounts of CaCO<sub>3</sub> (represented by orange color) and CaO (represented by green color).*

in which  $K_c$ , the “new” equilibrium constant, is now conveniently expressed in terms of a single concentration, that of  $\text{CO}_2$ . Keep in mind that the value of  $K_c$  does not depend on how much  $\text{CaCO}_3$  and  $\text{CaO}$  are present, as long as some of each is present at equilibrium (Figure 15.3).

The situation becomes simpler if we replace concentrations with activities. In thermodynamics, the activity of a pure solid is 1. Thus, the concentration terms for  $\text{CaCO}_3$  and  $\text{CaO}$  are both unity, and from the preceding equilibrium equation, we can immediately write  $K_c = [\text{CO}_2]$ . Similarly, the activity of a pure liquid is also 1. Thus, if a reactant or a product is a liquid, we can omit it in the equilibrium constant expression.

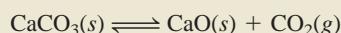
Alternatively, we can express the equilibrium constant as

$$K_P = P_{\text{CO}_2} \quad (15.8)$$

The equilibrium constant in this case is numerically equal to the pressure of  $\text{CO}_2$  gas, an easily measurable quantity.

## Example 15.4

Consider the following heterogeneous equilibrium:



At 800°C, the pressure of  $\text{CO}_2$  is 0.236 atm. Calculate (a)  $K_P$  and (b)  $K_c$  for the reaction at this temperature.

**Strategy** Remember that pure solids do not appear in the equilibrium constant expression. The relationship between  $K_P$  and  $K_c$  is given by Equation (15.5).

**Solution** (a) Using Equation (15.8) we write

$$K_P = P_{\text{CO}_2} \equiv 0.236$$

(b) From Equation (15.5), we know

$$K_B \equiv K_c(0.0821T)^{\Delta n}$$

(Continued)

In this case,  $T = 800 + 273 = 1073$  K and  $\Delta n = 1$ , so we substitute these values in the equation and obtain

$$0.236 = K_c(0.0821 \times 1073)$$

$$K_c = 2.68 \times 10^{-3}$$

**Similar problem:** 15.20.

**Practice Exercise** Consider the following equilibrium at 395 K:



The partial pressure of each gas is 0.265 atm. Calculate  $K_P$  and  $K_c$  for the reaction.

## The Form of $K$ and the Equilibrium Equation

Before closing this section, we should note these two important rules about writing equilibrium constants:

- When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant. Thus, if we write the  $\text{NO}_2-\text{N}_2\text{O}_4$  equilibrium at 25°C as



then

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 4.63 \times 10^{-3}$$

However, we can represent the equilibrium equally well as



and the equilibrium constant is now given by

$$K'_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{1}{K_c} = \frac{1}{4.63 \times 10^{-3}} = 216$$

You can see that  $K_c = 1/K'_c$  or  $K_c K'_c = 1.00$ . Either  $K_c$  or  $K'_c$  is a valid equilibrium constant, but it is meaningless to say that the equilibrium constant for the  $\text{NO}_2-\text{N}_2\text{O}_4$  system is  $4.63 \times 10^{-3}$ , or 216, unless we also specify how the equilibrium equation is written.

- The value of  $K$  also depends on how the equilibrium equation is balanced. Consider the following two ways of describing the same equilibrium:

$$\begin{aligned} \frac{1}{2}\text{N}_2\text{O}_4(g) &\rightleftharpoons \text{NO}_2(g) & K'_c &= \frac{[\text{NO}_2]}{[\text{N}_2\text{O}_4]^{1/2}} \\ \text{N}_2\text{O}_4(g) &\rightleftharpoons 2\text{NO}_2(g) & K_c &= \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \end{aligned}$$

Looking at the exponents we see that  $K'_c = \sqrt{K_c}$ . In Table 15.1 we find the average value of  $K_c = 4.63 \times 10^{-3}$ ; therefore,  $K'_c = 0.0680$ .

Thus, if you double a chemical equation throughout, the corresponding equilibrium constant will be the square of the original value; if you triple the equation, the equilibrium constant will be the cube of the original value, and so on. The  $\text{NO}_2-\text{N}_2\text{O}_4$  example illustrates once again the need to write the particular chemical equation when quoting the numerical value of an equilibrium constant.

## Summary of the Rules for Writing Equilibrium Constant Expressions

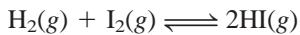
1. The concentrations of the reacting species in the condensed phase are expressed in moles per liter; in the gaseous phase, the concentrations can be expressed in moles per liter or in atmospheres.  $K_c$  is related to  $K_P$  by a simple equation [Equation (15.5)].
2. The concentrations of pure solids, pure liquids (in heterogeneous equilibria), and solvents (in homogeneous equilibria) do not appear in the equilibrium constant expressions.
3. The equilibrium constant ( $K_c$  or  $K_P$ ) is dimensionless.
4. In quoting a value for the equilibrium constant, we must specify the balanced equation and the temperature.

## 15.3 What Does the Equilibrium Constant Tell Us?

We have seen that the equilibrium constant for a given reaction can be calculated from known equilibrium concentrations. Once we know the value of the equilibrium constant, we can use Equation (15.2) to calculate unknown equilibrium concentrations—remembering, of course, that the equilibrium constant has a constant value only if the temperature does not change. In general, the equilibrium constant helps us to predict the direction in which a reaction mixture will proceed to achieve equilibrium and to calculate the concentrations of reactants and products once equilibrium has been reached. These uses of the equilibrium constant will be explored in this section.

### Predicting the Direction of a Reaction

The equilibrium constant  $K_c$  for the reaction

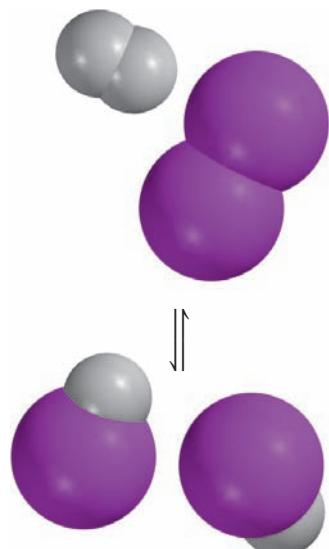


is 54.3 at 430°C. Suppose that in a certain experiment we place 0.243 mole of  $\text{H}_2$ , 0.146 mole of  $\text{I}_2$ , and 1.98 moles of  $\text{HI}$  all in a 1.00-L container at 430°C. Will there be a net reaction to form more  $\text{H}_2$  and  $\text{I}_2$  or more  $\text{HI}$ ? Inserting the starting concentrations in the equilibrium constant expression, we write

$$\frac{[\text{HI}]_0^2}{[\text{H}_2]_0[\text{I}_2]_0} = \frac{(1.98)^2}{(0.243)(0.146)} = 111$$

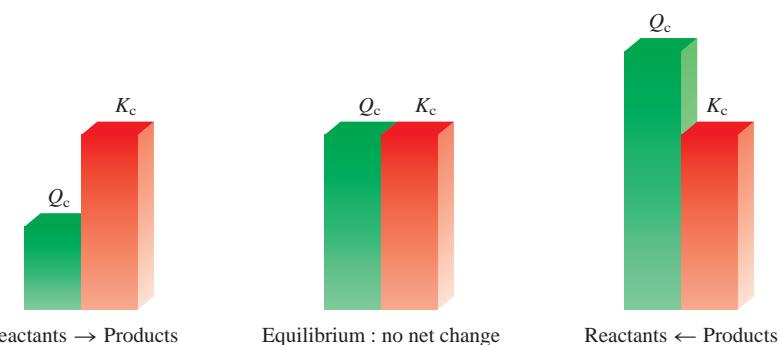
where the subscript 0 indicates initial concentrations. Because the calculated quotient  $[\text{HI}]_0^2/[\text{H}_2]_0[\text{I}_2]_0$  is greater than  $K_c$ , this system is not at equilibrium. Consequently, some of the  $\text{HI}$  will react to form more  $\text{H}_2$  and  $\text{I}_2$  (decreasing the value of the quotient). Thus, the net reaction proceeds from right to left to reach equilibrium.

*The quantity obtained by substituting the initial concentrations into the equilibrium constant expression is called the **reaction quotient** ( $Q_c$ ). To determine in which*



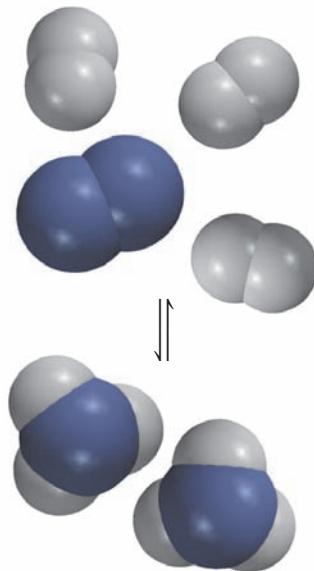
**Figure 15.4**

The direction of a reversible reaction to reach equilibrium depends on the relative magnitudes of  $Q_c$  and  $K_c$ .



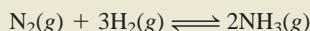
direction the net reaction will proceed to achieve equilibrium, we compare the values of  $Q_c$  and  $K_c$ . The three possible cases are as follows (Figure 15.4):

- $Q_c < K_c$  The ratio of initial concentrations of products to reactants is too small. To reach equilibrium, reactants must be converted to products. The system proceeds from left to right (consuming reactants, forming products) to reach equilibrium.
- $Q_c = K_c$  The initial concentrations are equilibrium concentrations. The system is at equilibrium.
- $Q_c > K_c$  The ratio of initial concentrations of products to reactants is too large. To reach equilibrium, products must be converted to reactants. The system proceeds from right to left (consuming products, forming reactants) to reach equilibrium.



### Example 15.5

At the start of a reaction, there are 0.249 mol  $\text{N}_2$ ,  $3.21 \times 10^{-2}$  mol  $\text{H}_2$ , and  $6.42 \times 10^{-4}$  mol  $\text{NH}_3$  in a 3.50-L reaction vessel at 375°C. If the equilibrium constant ( $K_c$ ) for the reaction



is 1.2 at this temperature, decide whether the system is at equilibrium. If it is not, predict which way the net reaction will proceed.

**Strategy** We are given the initial amounts of the gases (in moles) in a vessel of known volume (in liters), so we can calculate their molar concentrations and hence the reaction quotient ( $Q_c$ ). How does a comparison of  $Q_c$  with  $K_c$  enable us to determine if the system is at equilibrium or, if not, in which the direction the net reaction will proceed to reach equilibrium?

**Solution** The initial concentrations of the reacting species are

$$[\text{N}_2]_0 = \frac{0.249 \text{ mol}}{3.50 \text{ L}} = 0.0711 \text{ M}$$

$$[\text{H}_2]_0 = \frac{3.21 \times 10^{-2} \text{ mol}}{3.50 \text{ L}} = 9.17 \times 10^{-3} \text{ M}$$

$$[\text{NH}_3]_0 = \frac{6.42 \times 10^{-4} \text{ mol}}{3.50 \text{ L}} = 1.83 \times 10^{-4} \text{ M}$$

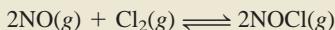
Next we write

$$Q_c = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} = \frac{(1.83 \times 10^{-4})^2}{(0.0711)(9.17 \times 10^{-3})^3} = 0.611$$

(Continued)

Because  $Q_c$  is smaller than  $K_c$  (1.2), the system is not at equilibrium. The net result will be an increase in the concentration of  $\text{NH}_3$  and a decrease in the concentrations of  $\text{N}_2$  and  $\text{H}_2$ . That is, the net reaction will proceed from left to right until equilibrium is reached.

**Practice Exercise** The equilibrium constant ( $K_c$ ) for the formation of nitrosyl chloride, an orange-yellow compound, from nitric oxide and molecular chlorine



is  $6.5 \times 10^4$  at  $35^\circ\text{C}$ . In a certain experiment,  $2.0 \times 10^{-2}$  mole of  $\text{NO}$ ,  $8.3 \times 10^{-3}$  mole of  $\text{Cl}_2$ , and 6.8 moles of  $\text{NOCl}$  are mixed in a 2.0-L flask. In which direction will the system proceed to reach equilibrium?

**Similar problem:** 15.21.

## Calculating Equilibrium Concentrations

If we know the equilibrium constant for a particular reaction, we can calculate the concentrations in the equilibrium mixture from a knowledge of the initial concentrations. Depending on the information given, the calculation may be straightforward or complex. In the most common situation, only the initial reactant concentrations are given. Let us consider this system involving a pair of geometric isomers in an organic solvent (Figure 15.5), which has an equilibrium constant ( $K_c$ ) of 24.0 at  $200^\circ\text{C}$ :



Suppose that only *cis*-stilbene is initially present at a concentration of 0.850 mol/L. How do we calculate the concentrations of *cis*- and *trans*-stilbene at equilibrium? From the stoichiometry of the reaction we see that for every mole of *cis*-stilbene converted, 1 mole of *trans*-stilbene is formed. Let  $x$  be the equilibrium concentration of *trans*-stilbene in moles per liter; therefore, the equilibrium concentration of *cis*-stilbene must be  $(0.850 - x)$  mol/L. It is useful to summarize the changes in concentration as

|                  | $\text{cis}$ -stilbene $\rightleftharpoons$ $\text{trans}$ -stilbene |      |
|------------------|--|------|
| Initial (M):     | 0.850  | 0    |
| Change (M):      | $-x$   | $+x$ |
| Equilibrium (M): | $(0.850 - x)$  | $x$  |

A positive (+) change represents an increase and a negative (−) change indicates a decrease in concentration at equilibrium. Next we set up the equilibrium constant expression

$$K_c = \frac{[\text{trans-stilbene}]}{[\text{cis-stilbene}]}$$

$$24.0 = \frac{x}{0.850 - x}$$

$$x = 0.816 \text{ M}$$

Having solved for  $x$ , we calculate the equilibrium concentrations of *cis*-stilbene and *trans*-stilbene as

$$[\text{cis-stilbene}] = (0.850 - 0.816) \text{ M} = 0.034 \text{ M}$$

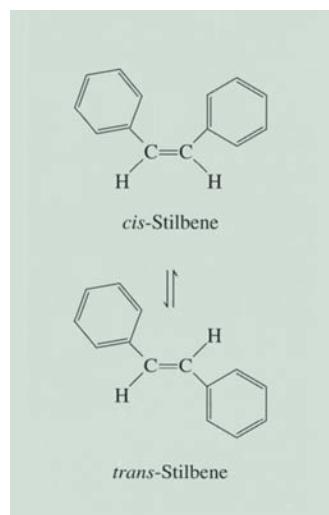
$$[\text{trans-stilbene}] = 0.816 \text{ M}$$



**Interactivity:**  
Determining Extent—  
Equilibrium Constant  
ARIS, Interactives



**Interactivity:**  
Determining Extent—  
Concentration from  
Equilibrium Expression  
ARIS, Interactives



**Figure 15.5**

The equilibrium between *cis*-stilbene and *trans*-stilbene. Note that both molecules have the same molecular formula ( $C_{14}\text{H}_{12}$ ) and also the same type of bonds. However, in *cis*-stilbene, the benzene rings are on one side of the  $\text{C}=\text{C}$  bond and the H atoms are on the other side whereas in *trans*-stilbene the benzene rings (and the H atoms) are across from the  $\text{C}=\text{C}$  bond. These compounds have different melting points and dipole moments.

We summarize our approach to solving equilibrium constant problems as

1. Express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown quantity  $x$ , which represents the change in concentration.
2. Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for  $x$ .
3. Having solved for  $x$ , calculate the equilibrium concentrations of all species.

### Example 15.6

A mixture of 0.500 mol  $\text{H}_2$  and 0.500 mol  $\text{I}_2$  was placed in a 1.00-L stainless-steel flask at 430°C. The equilibrium constant  $K_c$  for the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  is 54.3 at this temperature. Calculate the concentrations of  $\text{H}_2$ ,  $\text{I}_2$ , and  $\text{HI}$  at equilibrium.

**Strategy** We are given the initial amounts of the gases (in moles) in a vessel of known volume (in liters), so we can calculate their molar concentrations. Because initially no  $\text{HI}$  was present, the system could not be at equilibrium. Therefore, some  $\text{H}_2$  would react with the same amount of  $\text{I}_2$  (why?) to form  $\text{HI}$  until equilibrium was established.

**Solution** We follow the preceding procedure to calculate the equilibrium concentrations.

*Step 1:* The stoichiometry of the reaction is 1 mol  $\text{H}_2$  reacting with 1 mol  $\text{I}_2$  to yield 2 mol  $\text{HI}$ . Let  $x$  be the depletion in concentration (mol/L) of  $\text{H}_2$  and  $\text{I}_2$  at equilibrium. It follows that the equilibrium concentration of  $\text{HI}$  must be  $2x$ . We summarize the changes in concentrations as follows:

|                  | $\text{H}_2$  | + | $\text{I}_2$  | $\rightleftharpoons$ | $2\text{HI}$ |
|------------------|---------------|---|---------------|----------------------|--------------|
| Initial (M):     | 0.500         |   | 0.500         |                      | 0.000        |
| Change (M):      | $-x$          |   | $-x$          |                      | $+2x$        |
| Equilibrium (M): | $(0.500 - x)$ |   | $(0.500 - x)$ |                      | $2x$         |

*Step 2:* The equilibrium constant is given by

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

Substituting, we get

$$54.3 = \frac{(2x)^2}{(0.500 - x)(0.500 - x)}$$

Taking the square root of both sides, we get

$$\begin{aligned} 7.37 &= \frac{2x}{0.500 - x} \\ x &= 0.393 \text{ M} \end{aligned}$$

*Step 3:* At equilibrium, the concentrations are

$$[\text{H}_2] = (0.500 - 0.393) \text{ M} = 0.107 \text{ M}$$

$$[\text{I}_2] = (0.500 - 0.393) \text{ M} = 0.107 \text{ M}$$

$$[\text{HI}] = 2 \times 0.393 \text{ M} = 0.786 \text{ M}$$

(Continued)

This procedure for solving equilibrium concentrations is sometimes referred to as the ICE method, where the acronym stands for Initial, Change, and Equilibrium.

**Check** You can check your answers by calculating  $K_c$  using the equilibrium concentrations. Remember that  $K_c$  is a constant for a particular reaction at a given temperature.

**Similar problem:** 15.33.

**Practice Exercise** Consider the reaction in Example 15.6. Starting with a concentration of 0.040 M for HI, calculate the concentrations of HI, H<sub>2</sub>, and I<sub>2</sub> at equilibrium.

### Example 15.7

For the same reaction and temperature as in Example 15.6, suppose that the initial concentrations of H<sub>2</sub>, I<sub>2</sub>, and HI are 0.00623 M, 0.00414 M, and 0.0224 M, respectively. Calculate the concentrations of these species at equilibrium.

**Strategy** From the initial concentrations we can calculate the reaction quotient ( $Q_c$ ) to see if the system is at equilibrium or, if not, in which direction the net reaction will proceed to reach equilibrium. A comparison of  $Q_c$  with  $K_c$  also enables us to determine if there will be a depletion in H<sub>2</sub> and I<sub>2</sub> or HI as equilibrium is established.

**Solution** First we calculate  $Q_c$  as follows:

$$Q_c = \frac{[HI]_0^2}{[H_2]_0[I_2]_0} = \frac{(0.0224)^2}{(0.00623)(0.00414)} = 19.5$$

Because  $Q_c$  (19.5) is smaller than  $K_c$  (54.3), we conclude that the net reaction will proceed from left to right until equilibrium is reached (see Figure 15.3); that is, there will be a depletion of H<sub>2</sub> and I<sub>2</sub> and a gain in HI.

*Step 1:* Let  $x$  be the depletion in concentration (mol/L) of H<sub>2</sub> and I<sub>2</sub> at equilibrium.

From the stoichiometry of the reaction it follows that the increase in concentration for HI must be  $2x$ . Next we write

|                  |                  |   |                  |   |                  |
|------------------|------------------|---|------------------|---|------------------|
|                  | H <sub>2</sub>   | + | I <sub>2</sub>   | ↔ | 2HI              |
| Initial (M):     | 0.00623          |   | 0.00414          |   | 0.0224           |
| Change (M):      | - $x$            |   | - $x$            |   | + $2x$           |
| Equilibrium (M): | (0.00623 - $x$ ) |   | (0.00414 - $x$ ) |   | (0.0224 + $2x$ ) |

*Step 2:* The equilibrium constant is

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Substituting, we get

$$54.3 = \frac{(0.0224 + 2x)^2}{(0.00623 - x)(0.00414 - x)}$$

It is not possible to solve this equation by the square root shortcut, as the starting concentrations [H<sub>2</sub>] and [I<sub>2</sub>] are unequal. Instead, we must first carry out the multiplications

$$54.3(2.58 \times 10^{-5} - 0.0104x + x^2) = 5.02 \times 10^{-4} + 0.0896x + 4x^2$$

Collecting terms, we get

$$50.3x^2 - 0.654x + 8.98 \times 10^{-4} = 0$$

*(Continued)*

This is a quadratic equation of the form  $ax^2 + bx + c = 0$ . The solution for a quadratic equation (see Appendix 3) is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Here we have  $a = 50.3$ ,  $b = -0.654$ , and  $c = 8.98 \times 10^{-4}$ , so that

$$x = \frac{0.654 \pm \sqrt{(-0.654)^2 - 4(50.3)(8.98 \times 10^{-4})}}{2 \times 50.3}$$

$$x = 0.0114 \text{ M} \quad \text{or} \quad x = 0.00156 \text{ M}$$

The first solution is physically impossible because the amounts of  $\text{H}_2$  and  $\text{I}_2$  reacted would be more than those originally present. The second solution gives the correct answer. Note that in solving quadratic equations of this type, one answer is always physically impossible, so choosing a value for  $x$  is easy.

**Step 3:** At equilibrium, the concentrations are

$$[\text{H}_2] = (0.00623 - 0.00156) \text{ M} = 0.00467 \text{ M}$$

$$[\text{I}_2] = (0.00414 - 0.00156) \text{ M} = 0.00258 \text{ M}$$

$$[\text{HI}] = (0.0224 + 2 \times 0.00156) \text{ M} = 0.0255 \text{ M}$$

**Check** You can check the answers by calculating  $K_c$  using the equilibrium concentrations. Remember that  $K_c$  is a constant for a particular reaction at a given temperature.

**Similar problem:** 15.78.

**Practice Exercise** At 1280°C the equilibrium constant ( $K_c$ ) for the reaction



is  $1.1 \times 10^{-3}$ . If the initial concentrations are  $[\text{Br}_2] = 6.3 \times 10^{-2} \text{ M}$  and  $[\text{Br}] = 1.2 \times 10^{-2} \text{ M}$ , calculate the concentrations of these species at equilibrium.

## 15.4 Factors That Affect Chemical Equilibrium

Chemical equilibrium represents a balance between forward and reverse reactions. In most cases, this balance is quite delicate. Changes in experimental conditions may disturb the balance and shift the equilibrium position so that more or less of the desired product is formed. When we say that an equilibrium position shifts to the right, for example, we mean that the net reaction is now from left to right. At our disposal are the following experimentally controllable variables: concentration, pressure, volume, and temperature. Here we will examine how each of these variables affects a reacting system at equilibrium. In addition, we will examine the effect of a catalyst on equilibrium.

### Le Châtelier's Principle

There is a general rule that helps us to predict the direction in which an equilibrium reaction will move when a change in concentration, pressure, volume, or temperature occurs. The rule, known as **Le Châtelier's principle** (after the French chemist Henri Le Châtelier), states that *if an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as it tries to reestablish equilibrium*. The word "stress" here means a change in concentration, pressure,

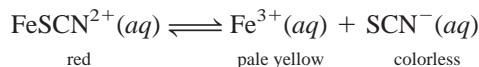


**Animation:**  
Le Châtelier's Principle  
ARIS, Animations

volume, or temperature that removes a system from the equilibrium state. We will use Le Châtelier's principle to assess the effects of such changes.

## Changes in Concentrations

Iron(III) thiocyanate  $[\text{Fe}(\text{SCN})_3]$  dissolves readily in water to give a red solution. The red color is due to the presence of hydrated  $\text{FeSCN}^{2+}$  ion. The equilibrium between undissociated  $\text{FeSCN}^{2+}$  and the  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  ions is given by



What happens if we add some sodium thiocyanate ( $\text{NaSCN}$ ) to this solution? In this case, the stress applied to the equilibrium system is an increase in the concentration of  $\text{SCN}^-$  (from the dissociation of  $\text{NaSCN}$ ). To offset this stress, some  $\text{Fe}^{3+}$  ions react with the added  $\text{SCN}^-$  ions, and the equilibrium shifts from right to left:



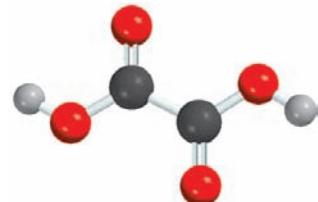
Consequently, the red color of the solution deepens (Figure 15.6). Similarly, if we added iron(III) nitrate  $[\text{Fe}(\text{NO}_3)_3]$  to the original solution, the red color would also deepen because the additional  $\text{Fe}^{3+}$  ions [from  $\text{Fe}(\text{NO}_3)_3$ ] would shift the equilibrium from right to left. Both  $\text{Na}^+$  and  $\text{NO}_3^-$  are colorless spectator ions.

Now suppose we add some oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) to the original solution. Oxalic acid ionizes in water to form the oxalate ion,  $\text{C}_2\text{O}_4^{2-}$ , which binds strongly to the  $\text{Fe}^{3+}$  ions. The formation of the stable yellow ion  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$  removes free  $\text{Fe}^{3+}$  ions from solution. Consequently, more  $\text{FeSCN}^{2+}$  units dissociate and the equilibrium shifts from left to right:



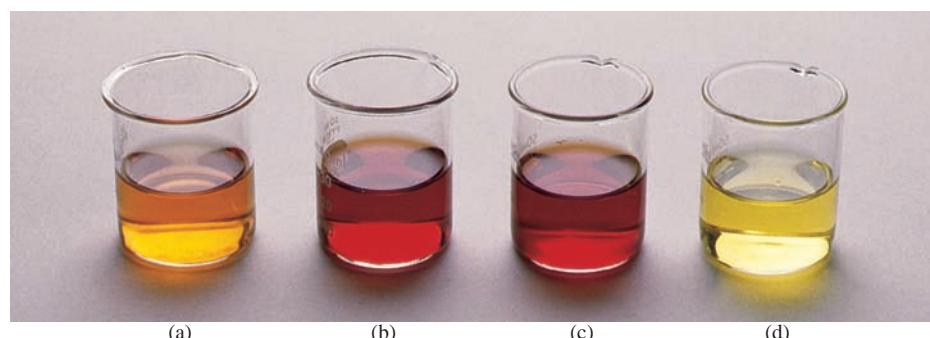
The red solution will turn yellow because of the formation of  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$  ions.

This experiment demonstrates that at equilibrium all reactants and products are present in the reacting system. Second, increasing the concentrations of the products ( $\text{Fe}^{3+}$  or  $\text{SCN}^-$ ) shifts the equilibrium to the left, and decreasing the concentration of the product  $\text{Fe}^{3+}$  shifts the equilibrium to the right. These results are just as predicted by Le Châtelier's principle.



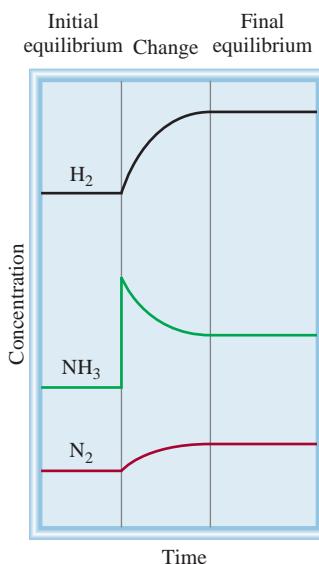
Oxalic acid is sometimes used to remove bathtub rings that consist of rust, or  $\text{Fe}_2\text{O}_3$ .

**Le Châtelier's principle simply summarizes the observed behavior of equilibrium systems; therefore, it is incorrect to say that a given equilibrium shift occurs "because of" Le Châtelier's principle.**



**Figure 15.6**

Effect of concentration change on the position of equilibrium. (a) An aqueous  $[\text{Fe}(\text{SCN})_3]$  solution. The color of the solution is due to both the red  $\text{FeSCN}^{2+}$  and the yellow  $\text{Fe}^{3+}$  species. (b) After the addition of some  $\text{NaSCN}$  to the solution in (a), the equilibrium shifts to the left. (c) After the addition of some  $\text{Fe}(\text{NO}_3)_3$  to the solution in (a), the equilibrium shifts to the left. (d) After the addition of some  $\text{H}_2\text{C}_2\text{O}_4$  to the solution in (a), the equilibrium shifts to the right. The yellow color is due to the  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$  ions.

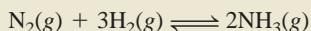


**Figure 15.7**  
Changes in concentration of  $H_2$ ,  $N_2$ , and  $NH_3$  after the addition of  $NH_3$  to the equilibrium mixture.

Similar problem: 15.36.

### Example 15.8

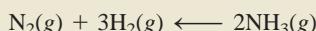
At 720°C, the equilibrium constant  $K_c$  for the reaction



is  $2.37 \times 10^{-3}$ . In a certain experiment, the equilibrium concentrations are  $[N_2] = 0.683\text{ M}$ ,  $[H_2] = 8.80\text{ M}$ , and  $[NH_3] = 1.05\text{ M}$ . Suppose some  $NH_3$  is added to the mixture so that its concentration is increased to  $3.65\text{ M}$ . (a) Use Le Châtelier's principle to predict the shift in direction of the net reaction to reach a new equilibrium. (b) Confirm your prediction by calculating the reaction quotient  $Q_c$  and comparing its value with  $K_c$ .

**Strategy** (a) What is the stress applied to the system? How does the system adjust to offset the stress? (b) At the instant when some  $NH_3$  is added, the system is no longer at equilibrium. How do we calculate the  $Q_c$  for the reaction at this point? How does a comparison of  $Q_c$  with  $K_c$  tell us the direction of the net reaction to reach equilibrium.

**Solution** (a) The stress applied to the system is the addition of  $NH_3$ . To offset this stress, some  $NH_3$  reacts to produce  $N_2$  and  $H_2$  until a new equilibrium is established. The net reaction therefore shifts from right to left; that is,



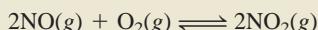
(b) At the instant when some of the  $NH_3$  is added, the system is no longer at equilibrium. The reaction quotient is given by

$$\begin{aligned} Q_c &= \frac{[NH_3]_0^2}{[N_2]_0[H_2]_0^3} \\ &= \frac{(3.65)^2}{(0.683)(8.80)^3} \\ &= 2.86 \times 10^{-2} \end{aligned}$$

Because this value is greater than  $2.37 \times 10^{-3}$ , the net reaction shifts from right to left until  $Q_c$  equals  $K_c$ .

Figure 15.7 shows qualitatively the changes in concentrations of the reacting species.

**Practice Exercise** At 430°C, the equilibrium constant ( $K_P$ ) for the reaction



is  $1.5 \times 10^5$ . In one experiment, the initial pressures of NO,  $O_2$ , and  $NO_2$  are  $2.1 \times 10^{-3}\text{ atm}$ ,  $1.1 \times 10^{-2}\text{ atm}$ , and  $0.14\text{ atm}$ , respectively. Calculate  $Q_P$  and predict the direction that the net reaction will shift to reach equilibrium.

## Changes in Pressure and Volume

Changes in pressure ordinarily do not affect the concentrations of reacting species in condensed phases (say, in an aqueous solution) because liquids and solids are virtually incompressible. On the other hand, concentrations of gases are greatly affected by changes in pressure. Let us look again at Equation (5.8):

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right)RT$$

Thus,  $P$  and  $V$  are related to each other inversely: The greater the pressure, the smaller the volume, and vice versa. Note, too, that the term  $(n/V)$  is the concentration of the gas in moles per liter, and it varies directly with pressure.

Suppose that the equilibrium system



is in a cylinder fitted with a movable piston. What happens if we increase the pressure on the gases by pushing down on the piston at constant temperature? As the volume decreases, the concentration ( $n/V$ ) of both  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  increases. Because the concentration of  $\text{NO}_2$  is squared, the increase in pressure increases the numerator more than the denominator. The system is no longer at equilibrium, so we write

$$Q_c = \frac{[\text{NO}_2]_0^2}{[\text{N}_2\text{O}_4]_0}$$

Thus,  $Q_c > K_c$ , and the net reaction will shift to the left until  $Q_c = K_c$  (Figure 15.8). Conversely, a decrease in pressure (increase in volume) would result in  $Q_c < K_c$ ; the net reaction would shift to the right until  $Q_c = K_c$ .

The shift in equilibrium can also be predicted using Le Châtelier's principle.

In general, an increase in pressure (decrease in volume) favors the net reaction that decreases the total number of moles of gases (the reverse reaction, in the preceding case), and a decrease in pressure (increase in volume) favors the net reaction that increases the total number of moles of gases (here, the forward reaction). For reactions in which there is no change in the number of moles of gases, for example,  $\text{H}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{HCl}(g)$ , a pressure (or volume) change has no effect on the position of equilibrium.

It is possible to change the pressure of a system without changing its volume. Suppose the  $\text{NO}_2$ - $\text{N}_2\text{O}_4$  system is contained in a stainless-steel vessel whose volume is constant. We can increase the total pressure in the vessel by adding an inert gas (helium, for example) to the equilibrium system. Adding helium to the equilibrium mixture at constant volume increases the total gas pressure and decreases the mole fractions of both  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ ; but the partial pressure of each gas, given by the product of its mole fraction and total pressure (see Section 5.5), does not change. Thus, the presence of an inert gas in such a case does not affect the equilibrium.

### Example 15.9

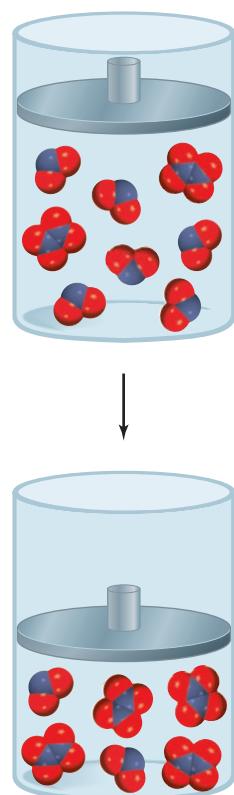
Consider the following equilibrium systems:

- $2\text{PbS}(s) + 3\text{O}_2(g) \rightleftharpoons 2\text{PbO}(s) + 2\text{SO}_2(g)$
- $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$
- $\text{H}_2(g) + \text{CO}_2(g) \rightleftharpoons \text{H}_2\text{O}(g) + \text{CO}(g)$

Predict the direction of the net reaction in each case as a result of increasing the pressure (decreasing the volume) on the system at constant temperature.

**Strategy** A change in pressure can affect only the volume of a gas, but not that of a solid because solids (and liquids) are much less compressible. The stress applied is an increase in pressure. According to Le Châtelier's principle, the system will adjust to partially offset this stress. In other words, the system will adjust to decrease the pressure. This can be achieved by shifting to the side of the equation that has fewer moles of gas. Recall that pressure is directly proportional to moles of gas:  $PV = nRT$  so  $P \propto n$ .

(Continued)



**Figure 15.8**  
Qualitative illustration of the effect of an increase in pressure on the  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$  equilibrium.

**Solution** (a) Consider only the gaseous molecules. In the balanced equation there are 3 moles of gaseous reactants and 2 moles of gaseous products. Therefore, the net reaction will shift toward the products (to the right) when the pressure is increased.

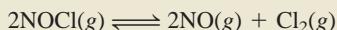
(b) The number of moles of products is 2 and that of reactants is 1; therefore, the net reaction will shift to the left, toward the reactant.

(c) The number of moles of products is equal to the number of moles of reactants, so a change in pressure has no effect on the equilibrium.

### **Similar problem: 15.46.**

**Check** In each case, the prediction is consistent with Le Châtelier's principle.

**Practice Exercise** Consider the equilibrium reaction involving nitrosyl chloride, nitric oxide, and molecular chlorine



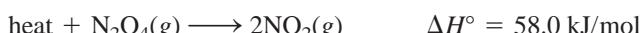
Predict the direction of the net reaction as a result of decreasing the pressure (increasing the volume) on the system at constant temperature.

# Changes in Temperature

A change in concentration, pressure, or volume may alter the equilibrium position, that is, the relative amounts of reactants and products, but it does not change the value of the equilibrium constant. Only a change in temperature can alter the equilibrium constant. To see why, let us consider the reaction



The forward reaction is endothermic (absorbs heat,  $\Delta H^\circ > 0$ ):



so the reverse reaction is exothermic (releases heat,  $\Delta H^\circ < 0$ ):

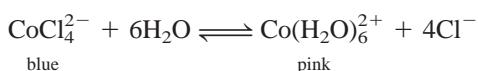


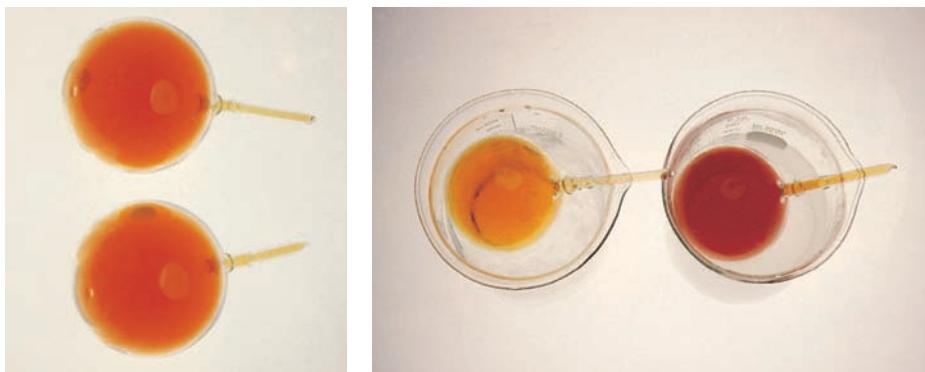
At equilibrium at a certain temperature, the heat effect is zero because there is no net reaction. If we treat heat as though it were a chemical reagent, then a rise in temperature “adds” heat to the system and a drop in temperature “removes” heat from the system. As with a change in any other parameter (concentration, pressure, or volume), the system shifts to reduce the effect of the change. Therefore, a temperature increase favors the endothermic direction (from left to right of the equilibrium equation), which decreases  $[N_2O_4]$  and increases  $[NO_2]$ . A temperature decrease favors the exothermic direction (from right to left of the equilibrium equation), which decreases  $[NO_2]$  and increases  $[N_2O_4]$ . Consequently, the equilibrium constant, given by

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

increases when the system is heated and decreases when the system is cooled (Figure 15.9).

As another example, consider the equilibrium between the following ions:



**Figure 15.9**

(a) Two bulbs containing a mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  gases at equilibrium at room temperature. (b) When one bulb is immersed in ice water (left), its color becomes lighter, indicating the formation of colorless  $\text{N}_2\text{O}_4$  gas. When the other bulb is immersed in hot water, its color darkens, indicating an increase in  $\text{NO}_2$ .

The formation of  $\text{CoCl}_4^{2-}$  is endothermic. On heating, the equilibrium shifts to the left and the solution turns blue. Cooling favors the exothermic reaction [the formation of  $\text{Co}(\text{H}_2\text{O})_6^{2+}$ ] and the solution turns pink (Figure 15.10).

In summary, *a temperature increase favors an endothermic reaction, and a temperature decrease favors an exothermic reaction.*

### The Effect of a Catalyst

We know that a catalyst enhances the rate of a reaction by lowering the reaction's activation energy (Section 14.4). However, as Figure 14.17 shows, a catalyst lowers the activation energy of the forward reaction and the reverse reaction to the same extent. We can therefore conclude that the presence of a catalyst does not alter the equilibrium constant, nor does it shift the position of an equilibrium system. Adding a catalyst to a reaction mixture that is not at equilibrium will simply cause the mixture to reach equilibrium sooner. The same equilibrium mixture could be obtained without the catalyst, but we might have to wait much longer for it to happen.

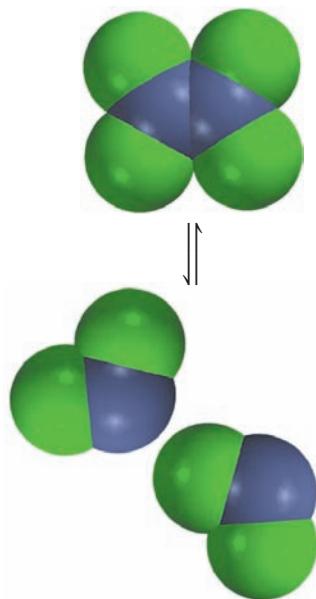
### Summary of Factors That May Affect the Equilibrium Position

We have considered four ways to affect a reacting system at equilibrium. It is important to remember that, of the four, *only a change in temperature changes the value of the equilibrium constant*. Changes in concentration, pressure, and volume can alter

**Figure 15.10**

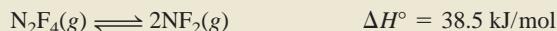
(Left) Heating favors the formation of the blue  $\text{CoCl}_4^{2-}$  ion. (Right) Cooling favors the formation of the pink  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  ion.

the equilibrium concentrations of the reacting mixture, but they cannot change the equilibrium constant as long as the temperature does not change. A catalyst can speed up the process, but it has no effect on the equilibrium constant or on the equilibrium concentrations of the reacting species.



### Example 15.10

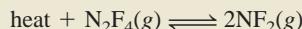
Consider the following equilibrium process between dinitrogen tetrafluoride (N<sub>2</sub>F<sub>4</sub>) and nitrogen difluoride (NF<sub>2</sub>):



Predict the changes in the equilibrium if (a) the reacting mixture is heated at constant volume; (b) some N<sub>2</sub>F<sub>4</sub> gas is removed from the reacting mixture at constant temperature and volume; (c) the pressure on the reacting mixture is decreased at constant temperature; and (d) a catalyst is added to the reacting mixture.

**Strategy** (a) What does the sign of  $\Delta H^\circ$  indicate about the heat change (endothermic or exothermic) for the forward reaction? (b) Would the removal of some N<sub>2</sub>F<sub>4</sub> increase or decrease the  $Q_c$  of the reaction? (c) How would the decrease in pressure change the volume of the system? (d) What is the function of a catalyst? How does it affect a reacting system not at equilibrium? at equilibrium?

**Solution** (a) The stress applied is the heat added to the system. Note that the  $\text{N}_2\text{F}_4 \longrightarrow 2\text{NF}_2$  reaction is an endothermic process ( $\Delta H^\circ > 0$ ), which absorbs heat from the surroundings. Therefore, we can think of heat as a reactant



The system will adjust to remove some of the added heat by undergoing a decomposition reaction (from left to right). The equilibrium constant

$$K_c = \frac{[\text{NF}_2]^2}{[\text{N}_2\text{F}_4]}$$

will therefore increase with increasing temperature because the concentration of NF<sub>2</sub> has increased and that of N<sub>2</sub>F<sub>4</sub> has decreased. Recall that the equilibrium constant is a constant only at a particular temperature. If the temperature is changed, then the equilibrium constant will also change.

(b) The stress here is the removal of N<sub>2</sub>F<sub>4</sub> gas. The system will shift to replace some of the N<sub>2</sub>F<sub>4</sub> removed. Therefore, the system shifts from right to left until equilibrium is reestablished. As a result, some NF<sub>2</sub> combines to form N<sub>2</sub>F<sub>4</sub>.

**Comment** The equilibrium constant remains unchanged in this case because temperature is held constant. It might seem that  $K_c$  should change because NF<sub>2</sub> combines to produce N<sub>2</sub>F<sub>4</sub>. Remember, however, that initially some N<sub>2</sub>F<sub>4</sub> was removed. The system adjusts to replace only some of the N<sub>2</sub>F<sub>4</sub> that was removed, so that overall the amount of N<sub>2</sub>F<sub>4</sub> has decreased. In fact, by the time the equilibrium is reestablished, the amounts of both NF<sub>2</sub> and N<sub>2</sub>F<sub>4</sub> have decreased. Looking at the equilibrium constant expression, we see that dividing a smaller numerator by a smaller denominator gives the same value of  $K_c$ .

(c) The stress applied is a decrease in pressure (which is accompanied by an increase in gas volume). The system will adjust to remove the stress by increasing the pressure. Recall that pressure is directly proportional to the number of moles of a gas. In the balanced equation, we see that the formation of NF<sub>2</sub> from N<sub>2</sub>F<sub>4</sub> will increase

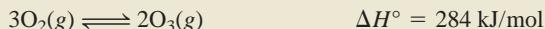
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the total number of moles of gases and hence the pressure. Therefore, the system will shift from left to right to reestablish equilibrium. The equilibrium constant will remain unchanged because temperature is held constant.

- (d) The function of a catalyst is to increase the rate of a reaction. If a catalyst is added to a reacting system not at equilibrium, the system will reach equilibrium faster than if left undisturbed. If a system is already at equilibrium, as in this case, the addition of a catalyst will not affect either the concentrations of  $\text{NF}_2$  and  $\text{N}_2\text{F}_4$  or the equilibrium constant.

**Similar problems:** 15.47, 15.48.

**Practice Exercise** Consider the equilibrium between molecular oxygen and ozone



What would be the effect of (a) increasing the pressure on the system by decreasing the volume, (b) adding  $\text{O}_2$  to the system, (c) decreasing the temperature, and (d) adding a catalyst?

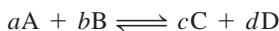
## KEY EQUATIONS

$$K = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \quad (15.2) \quad \text{Law of mass action. General expression of equilibrium constant.}$$

$$K_P = K_c(0.0821T)^{\Delta n} \quad (15.5) \quad \text{Relationship between } K_P \text{ and } K_c.$$

## SUMMARY OF FACTS AND CONCEPTS

- Dynamic equilibria between phases are called physical equilibria. Chemical equilibrium is a reversible process in which the rates of the forward and reverse reactions are equal and the concentrations of reactants and products do not change with time.
- For the general chemical reaction



the concentrations of reactants and products at equilibrium (in moles per liter) are related by the equilibrium constant expression [Equation (15.2)].

- The equilibrium constant for gases,  $K_P$ , expresses the relationship of the equilibrium partial pressures (in atm) of reactants and products.
- A chemical equilibrium process in which all reactants and products are in the same phase is homogeneous. If the reactants and products are not all in the same phase, the equilibrium is heterogeneous. The concentrations of pure solids, pure liquids, and solvents are constant and do not appear in the equilibrium constant expression of a reaction.

- The value of  $K$  depends on how the chemical equation is balanced, and the equilibrium constant for the reverse of a particular reaction is the reciprocal of the equilibrium constant of that reaction.
- The equilibrium constant is the ratio of the rate constant for the forward reaction to that for the reverse reaction.
- The reaction quotient  $Q$  has the same form as the equilibrium constant, but it applies to a reaction that may not be at equilibrium. If  $Q > K$ , the reaction will proceed from right to left to achieve equilibrium. If  $Q < K$ , the reaction will proceed from left to right to achieve equilibrium.
- Le Châtelier's principle states that if an external stress is applied to a system at chemical equilibrium, the system will adjust to partially offset the stress.
- Only a change in temperature changes the value of the equilibrium constant for a particular reaction. Changes in concentration, pressure, or volume may change the equilibrium concentrations of reactants and products. The addition of a catalyst hastens the attainment of equilibrium but does not affect the equilibrium concentrations of reactants and products.

## KEY WORDS

Chemical equilibrium, p. 497  
Equilibrium constant, p. 499

Heterogeneous equilibrium, p. 504  
Homogeneous equilibrium, p. 500

Le Châtelier's principle, p. 512  
Physical equilibrium, p. 497

Reaction quotient ( $Q_c$ ), p. 507

## QUESTIONS AND PROBLEMS

### Concept of Equilibrium

#### *Review Questions*

- 15.1 Define equilibrium. Give two examples of a dynamic equilibrium.
- 15.2 Explain the difference between physical equilibrium and chemical equilibrium. Give two examples of each.
- 15.3 Briefly describe the importance of equilibrium in the study of chemical reactions.
- 15.4 Consider the equilibrium system  $3A \rightleftharpoons B$ . Sketch the change in concentrations of A and B with time for these situations: (a) Initially only A is present; (b) initially only B is present; (c) initially both A and B are present (with A in higher concentration). In each case, assume that the concentration of B is higher than that of A at equilibrium.

### Equilibrium Constant Expressions

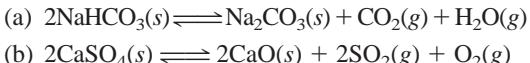
#### *Review Questions*

- 15.5 Define homogeneous equilibrium and heterogeneous equilibrium. Give two examples of each.
- 15.6 What do the symbols  $K_c$  and  $K_P$  represent?

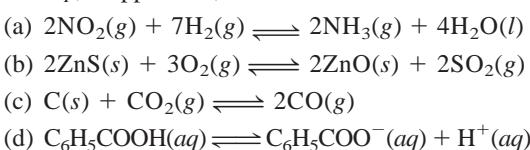
#### *Problems*

- 15.7 Write equilibrium constant expressions for  $K_c$  and for  $K_P$ , if applicable, for these processes:
  - (a)  $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$
  - (b)  $3O_2(g) \rightleftharpoons 2O_3(g)$
  - (c)  $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$
  - (d)  $H_2O(g) + C(s) \rightleftharpoons CO(g) + H_2(g)$
  - (e)  $HCOOH(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$
  - (f)  $2HgO(s) \rightleftharpoons 2Hg(l) + O_2(g)$

- 15.8** Write the expressions for the equilibrium constants  $K_P$  of these thermal decompositions:



- 15.9** Write the equilibrium constant expressions for  $K_c$  and  $K_P$ , if applicable, for these reactions:



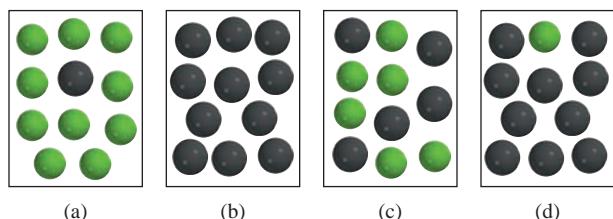
### Calculating Equilibrium Constants

#### *Review Question*

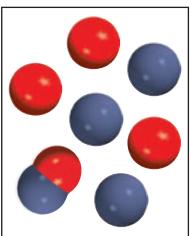
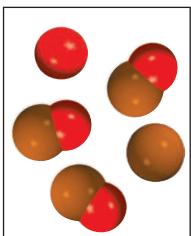
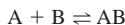
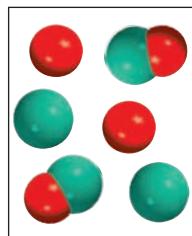
- 15.10** Write the equation relating  $K_c$  and  $K_P$  and define all the terms.

#### *Problems*

- 15.11** The equilibrium constant for the reaction  $A \rightleftharpoons B$  is  $K_c = 10$  at a certain temperature. (1) Starting with only reactant A, which of the diagrams best represents the system at equilibrium? (2) Which of the diagrams best represents the system at equilibrium if  $K_c = 0.10$ ? Explain why you can calculate  $K_c$  in each case without knowing the volume of the container. The gray spheres represent the A molecules and the green spheres represent the B molecules.



- 15.12** The following diagrams represent the equilibrium state for three different reactions of the type  $A + X \rightleftharpoons AX$  ( $X = B, C$ , or  $D$ ):

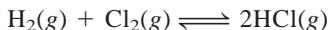


- (a) Which reaction has the largest equilibrium constant? (b) Which reaction has the smallest equilibrium constant?

- 15.13** The equilibrium constant ( $K_c$ ) for the reaction

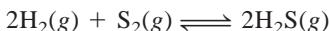


is  $4.17 \times 10^{-34}$  at  $25^\circ\text{C}$ . What is the equilibrium constant for the reaction



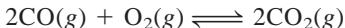
at the same temperature?

- 15.14** Consider the following equilibrium process at  $700^\circ\text{C}$ :



Analysis shows that there are 2.50 moles of  $\text{H}_2$ ,  $1.35 \times 10^{-5}$  mole of  $\text{S}_2$ , and 8.70 moles of  $\text{H}_2\text{S}$  present in a 12.0-L flask at equilibrium. Calculate the equilibrium constant  $K_c$  for the reaction.

- 15.15** What is the  $K_P$  at  $1273^\circ\text{C}$  for the reaction



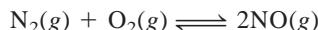
if  $K_c$  is  $2.24 \times 10^{22}$  at the same temperature?

- 15.16** The equilibrium constant  $K_P$  for the reaction



if  $5.0 \times 10^{-4}$  at  $302^\circ\text{C}$ . What is  $K_c$  for this reaction?

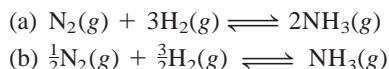
- 15.17** Consider this reaction:



If the equilibrium partial pressures of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  are 0.15 atm, 0.33 atm, and 0.050 atm, respectively, at  $2200^\circ\text{C}$ , what is  $K_P$ ?

- 15.18** A reaction vessel contains  $\text{NH}_3$ ,  $\text{N}_2$ , and  $\text{H}_2$  at equilibrium at a certain temperature. The equilibrium concentrations are  $[\text{NH}_3] = 0.25\text{ M}$ ,  $[\text{N}_2] = 0.11\text{ M}$ , and  $[\text{H}_2] = 1.91\text{ M}$ . Calculate the equilibrium con-

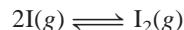
stant  $K_c$  for the synthesis of ammonia if the reaction is represented as



- 15.19** The equilibrium constant  $K_c$  for the reaction



is  $3.8 \times 10^{-5}$  at  $727^\circ\text{C}$ . Calculate  $K_c$  and  $K_P$  for the equilibrium



at the same temperature.

- 15.20** The pressure of the reacting mixture



at equilibrium is 0.105 atm at  $350^\circ\text{C}$ . Calculate  $K_P$  and  $K_c$  for this reaction.

- 15.21** The equilibrium constant  $K_P$  for the reaction



is 1.05 at  $250^\circ\text{C}$ . The reaction starts with a mixture of  $\text{PCl}_5$ ,  $\text{PCl}_3$ , and  $\text{Cl}_2$  at pressures of 0.177 atm, 0.223 atm, and 0.111 atm, respectively, at  $250^\circ\text{C}$ . When the mixture comes to equilibrium at that temperature, which pressures will have decreased and which will have increased? Explain why.

- 15.22** Ammonium carbamate,  $\text{NH}_4\text{CO}_2\text{NH}_2$ , decomposes as



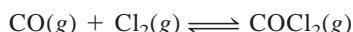
Starting with only the solid, it is found that at  $40^\circ\text{C}$  the total gas pressure ( $\text{NH}_3$  and  $\text{CO}_2$ ) is 0.363 atm. Calculate the equilibrium constant  $K_P$ .

- 15.23** Consider the following reaction at  $1600^\circ\text{C}$ :

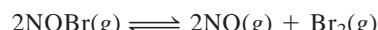


When 1.05 moles of  $\text{Br}_2$  are put in a 0.980-L flask, 1.20 percent of the  $\text{Br}_2$  undergoes dissociation. Calculate the equilibrium constant  $K_c$  for the reaction.

- 15.24** Pure phosgene gas ( $\text{COCl}_2$ ),  $3.00 \times 10^{-2}$  mol, was placed in a 1.50-L container. It was heated to  $800\text{ K}$ , and at equilibrium the pressure of  $\text{CO}$  was found to be 0.497 atm. Calculate the equilibrium constant  $K_P$  for the reaction



- 15.25** Consider the equilibrium



If nitrosyl bromide,  $\text{NOBr}$ , is 34 percent dissociated at  $25^\circ\text{C}$  and the total pressure is 0.25 atm, calculate  $K_P$  and  $K_c$  for the dissociation at this temperature.

- 15.26** A 2.50-mol quantity of NOCl was initially placed in a 1.50-L reaction chamber at 400°C. After equilibrium was established, it was found that 28.0 percent of the NOCl had dissociated:



Calculate the equilibrium constant  $K_c$  for the reaction.

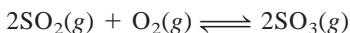
## Calculating Equilibrium Concentrations

### Review Questions

- 15.27 Define reaction quotient. How does it differ from equilibrium constant?
- 15.28 Outline the steps for calculating the concentrations of reacting species in an equilibrium reaction.

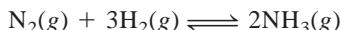
### Problems

- 15.29 The equilibrium constant  $K_P$  for the reaction



is  $5.60 \times 10^4$  at 350°C. SO<sub>2</sub> and O<sub>2</sub> are mixed initially at 0.350 atm and 0.762 atm, respectively, at 350°C. When the mixture equilibrates, is the total pressure less than or greater than the sum of the initial pressures, 1.112 atm?

- 15.30 For the synthesis of ammonia



the equilibrium constant  $K_c$  at 375°C is 1.2. Starting with [H<sub>2</sub>]<sub>0</sub> = 0.76 M, [N<sub>2</sub>]<sub>0</sub> = 0.60 M, and [NH<sub>3</sub>]<sub>0</sub> = 0.48 M, when this mixture comes to equilibrium, which gases will have increased in concentration and which will have decreased in concentration?

- 15.31 For the reaction



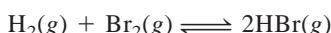
at 700°C,  $K_c$  = 0.534. Calculate the number of moles of H<sub>2</sub> formed at equilibrium if a mixture of 0.300 mole of CO and 0.300 mole of H<sub>2</sub>O is heated to 700°C in a 10.0-L container.

- 15.32 A sample of pure NO<sub>2</sub> gas heated to 1000 K decomposes:



The equilibrium constant  $K_P$  is 158. Analysis shows that the partial pressure of O<sub>2</sub> is 0.25 atm at equilibrium. Calculate the pressure of NO and NO<sub>2</sub> in the mixture.

- 15.33 The equilibrium constant  $K_c$  for the reaction



is  $2.18 \times 10^6$  at 730°C. Starting with 3.20 moles HBr in a 12.0-L reaction vessel, calculate the concentrations of H<sub>2</sub>, Br<sub>2</sub>, and HBr at equilibrium.

- 15.34 The dissociation of molecular iodine into iodine atoms is represented as



At 1000 K, the equilibrium constant  $K_c$  for the reaction is  $3.80 \times 10^{-5}$ . Suppose you start with 0.0456 mole of I<sub>2</sub> in a 2.30-L flask at 1000 K. What are the concentrations of the gases at equilibrium?

- 15.35 The equilibrium constant  $K_c$  for the decomposition of phosgene, COCl<sub>2</sub>, is  $4.63 \times 10^{-3}$  at 527°C:



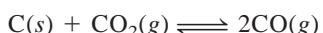
Calculate the equilibrium partial pressure of all the components, starting with pure phosgene at 0.760 atm.

- 15.36 Consider this equilibrium process at 686°C:



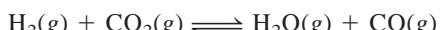
The equilibrium concentrations of the reacting species are [CO] = 0.050 M, [H<sub>2</sub>] = 0.045 M, [CO<sub>2</sub>] = 0.086 M, and [H<sub>2</sub>O] = 0.040 M. (a) Calculate  $K_c$  for the reaction at 686°C. (b) If the concentration of CO<sub>2</sub> were raised to 0.50 mol/L by the addition of CO<sub>2</sub>, what would be the concentrations of all the gases when equilibrium is reestablished?

- 15.37 Consider the heterogeneous equilibrium process:



At 700°C, the total pressure of the system is found to be 4.50 atm. If the equilibrium constant  $K_P$  is 1.52, calculate the equilibrium partial pressures of CO<sub>2</sub> and CO.

- 15.38 The equilibrium constant  $K_c$  for the reaction



is 4.2 at 1650°C. Initially 0.80 mol H<sub>2</sub> and 0.80 mol CO<sub>2</sub> are injected into a 5.0-L flask. Calculate the concentration of each species at equilibrium.

## Le Châtelier's Principle

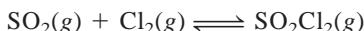
### Review Questions

- 15.39 Explain Le Châtelier's principle. How can this principle help us maximize the yields of reactions?
- 15.40 Use Le Châtelier's principle to explain why the equilibrium vapor pressure of a liquid increases with increasing temperature.
- 15.41 List four factors that can shift the position of an equilibrium. Which one can alter the value of the equilibrium constant?

- 15.42 What is meant by “the position of an equilibrium”? Does the addition of a catalyst have any effects on the position of an equilibrium?

### Problems

- 15.43 Consider this equilibrium system:



Predict how the equilibrium position would change if (a)  $\text{Cl}_2$  gas were added to the system, (b)  $\text{SO}_2\text{Cl}_2$  were removed from the system, (c)  $\text{SO}_2$  were removed from the system. The temperature remains constant.

- 15.44** Heating solid sodium bicarbonate in a closed vessel established this equilibrium:



What would happen to the equilibrium position if (a) some of the  $\text{CO}_2$  were removed from the system, (b) some solid  $\text{Na}_2\text{CO}_3$  were added to the system, (c) some of the solid  $\text{NaHCO}_3$  were removed from the system? The temperature remains constant.

- 15.45 Consider these equilibrium systems:

- (a)  $\text{A} \rightleftharpoons 2\text{B}$   $\Delta H^\circ = 20.0 \text{ kJ/mol}$
- (b)  $\text{A} + \text{B} \rightleftharpoons \text{C}$   $\Delta H^\circ = -5.4 \text{ kJ/mol}$
- (c)  $\text{A} \rightleftharpoons \text{B}$   $\Delta H^\circ = 0.0 \text{ kJ/mol}$

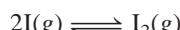
Predict the change in the equilibrium constant  $K_c$  that would occur in each case if the temperature of the reacting system were raised.

- 15.46** What effect does an increase in pressure have on each of these systems at equilibrium?

- (a)  $\text{A}(s) \rightleftharpoons 2\text{B}(s)$
- (b)  $2\text{A}(l) \rightleftharpoons \text{B}(l)$
- (c)  $\text{A}(s) \rightleftharpoons \text{B}(g)$
- (d)  $\text{A}(g) \rightleftharpoons \text{B}(g)$
- (e)  $\text{A}(g) \rightleftharpoons 2\text{B}(g)$

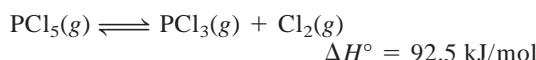
The temperature is kept constant. In each case, the reacting mixture is in a cylinder fitted with a movable piston.

- 15.47 Consider the equilibrium



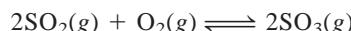
What would be the effect on the position of equilibrium of (a) increasing the total pressure on the system by decreasing its volume, (b) adding  $\text{I}_2$  to the reaction mixture, (c) decreasing the temperature?

- 15.48** Consider this equilibrium process:



Predict the direction of the shift in equilibrium when (a) the temperature is raised, (b) more chlorine gas is added to the reaction mixture, (c) some  $\text{PCl}_3$  is removed from the mixture, (d) the pressure on the gases is increased, (e) a catalyst is added to the reaction mixture.

- 15.49 Consider the reaction



$$\Delta H^\circ = -198.2 \text{ kJ/mol}$$

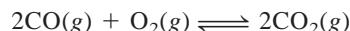
Comment on the changes in the concentrations of  $\text{SO}_2$ ,  $\text{O}_2$ , and  $\text{SO}_3$  at equilibrium if we were to (a) increase the temperature, (b) increase the pressure, (c) increase  $\text{SO}_2$ , (d) add a catalyst, (e) add helium at constant volume.

- 15.50** In the uncatalyzed reaction



at  $100^\circ\text{C}$  the pressures of the gases at equilibrium are  $P_{\text{N}_2\text{O}_4} = 0.377 \text{ atm}$  and  $P_{\text{NO}_2} = 1.56 \text{ atm}$ . What would happen to these pressures if a catalyst were present?

- 15.51 Consider the gas-phase reaction



Predict the shift in the equilibrium position when helium gas is added to the equilibrium mixture (a) at constant pressure and (b) at constant volume.

- 15.52** Consider this reaction at equilibrium in a closed container:

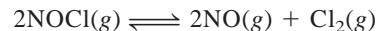


What would happen if (a) the volume is increased, (b) some  $\text{CaO}$  is added to the mixture, (c) some  $\text{CaCO}_3$  is removed, (d) some  $\text{CO}_2$  is added to the mixture, (e) a few drops of an  $\text{NaOH}$  solution are added to the mixture, (f) a few drops of an  $\text{HCl}$  solution are added to the mixture (ignore the reaction between  $\text{CO}_2$  and water), (g) the temperature is increased?

### Additional Problems

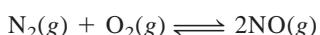
- 15.53 Consider the statement: The equilibrium constant of a reacting mixture of solid  $\text{NH}_4\text{Cl}$  and gaseous  $\text{NH}_3$  and  $\text{HCl}$  is 0.316. List three important pieces of information that are missing from this statement.

- 15.54** Pure  $\text{NOCl}$  gas was heated at  $240^\circ\text{C}$  in a 1.00-L container. At equilibrium the total pressure was 1.00 atm and the  $\text{NOCl}$  pressure was 0.64 atm.



- (a) Calculate the partial pressures of  $\text{NO}$  and  $\text{Cl}_2$  in the system. (b) Calculate the equilibrium constant  $K_P$ .

- 15.55 Consider this reaction:



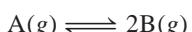
The equilibrium constant  $K_P$  for the reaction is  $1.0 \times 10^{-15}$  at  $25^\circ\text{C}$  and 0.050 at  $2200^\circ\text{C}$ . Is the formation of nitric oxide endothermic or exothermic? Explain your answer.

- 15.56 Baking soda (sodium bicarbonate) undergoes thermal decomposition as



Would we obtain more  $\text{CO}_2$  and  $\text{H}_2\text{O}$  by adding extra baking soda to the reaction mixture in (a) a closed vessel or (b) an open vessel?

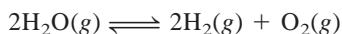
- 15.57 Consider the following reaction at equilibrium:



From the following data, calculate the equilibrium constant (both  $K_P$  and  $K_c$ ) at each temperature. Is the reaction endothermic or exothermic?

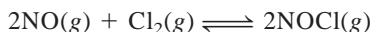
| Temperature ( $^\circ\text{C}$ ) | [A]    | [B]   |
|----------------------------------|--------|-------|
| 200                              | 0.0125 | 0.843 |
| 300                              | 0.171  | 0.764 |
| 400                              | 0.250  | 0.724 |

- 15.58 The equilibrium constant  $K_P$  for the reaction



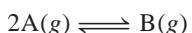
is found to be  $2 \times 10^{-42}$  at  $25^\circ\text{C}$ . (a) What is  $K_c$  for the reaction at the same temperature? (b) The very small value of  $K_P$  (and  $K_c$ ) indicates that the reaction overwhelmingly favors the formation of water molecules. Explain why, despite this fact, a mixture of hydrogen and oxygen gases can be kept at room temperature without any change.

- 15.59 Consider the following reacting system:



What combination of temperature and pressure (high or low) would maximize the yield of  $\text{NOCl}$ ? [Hint:  $\Delta H_f^\circ(\text{NOCl}) = 51.7 \text{ kJ/mol}$ . You will also need to consult Appendix 2.]

- 15.60 At a certain temperature and a total pressure of 1.2 atm, the partial pressures of an equilibrium mixture



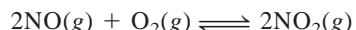
are  $P_A = 0.60 \text{ atm}$  and  $P_B = 0.60 \text{ atm}$ . (a) Calculate the  $K_P$  for the reaction at this temperature. (b) If the total pressure were increased to 1.5 atm, what would be the partial pressures of A and B at equilibrium?

- 15.61 The decomposition of ammonium hydrogen sulfide



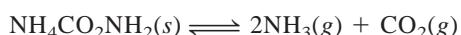
is an endothermic process. A 6.1589-g sample of the solid is placed in an evacuated 4.000-L vessel at exactly  $24^\circ\text{C}$ . After equilibrium has been established, the total pressure inside is 0.709 atm. Some solid  $\text{NH}_4\text{HS}$  remains in the vessel. (a) What is the  $K_P$  for the reaction? (b) What percentage of the solid has decomposed? (c) If the volume of the vessel were doubled at constant temperature, what would happen to the amount of solid in the vessel?

- 15.62 Consider the reaction



At  $430^\circ\text{C}$ , an equilibrium mixture consists of 0.020 mole of  $\text{O}_2$ , 0.040 mole of  $\text{NO}$ , and 0.96 mole of  $\text{NO}_2$ . Calculate  $K_P$  for the reaction, given that the total pressure is 0.20 atm.

- 15.63 When heated, ammonium carbamate decomposes as



At a certain temperature the equilibrium pressure of the system is 0.318 atm. Calculate  $K_P$  for the reaction.

- 15.64 A mixture of 0.47 mole of  $\text{H}_2$  and 3.59 moles of  $\text{HCl}$  is heated to  $2800^\circ\text{C}$ . Calculate the equilibrium partial pressures of  $\text{H}_2$ ,  $\text{Cl}_2$ , and  $\text{HCl}$  if the total pressure is 2.00 atm. The  $K_P$  for the reaction  $\text{H}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{HCl}(g)$  is 193 at  $2800^\circ\text{C}$ .

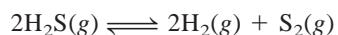
- 15.65 Consider the reaction in a closed container:



Initially, 1 mole of  $\text{N}_2\text{O}_4$  is present. At equilibrium,  $\alpha$  mole of  $\text{N}_2\text{O}_4$  has dissociated to form  $\text{NO}_2$ . (a) Derive an expression for  $K_P$  in terms of  $\alpha$  and  $P$ , the total pressure. (b) How does the expression in (a) help you predict the shift in equilibrium caused by an increase in  $P$ ? Does your prediction agree with Le Châtelier's principle?

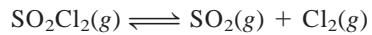
- 15.66 One mole of  $\text{N}_2$  and 3 moles of  $\text{H}_2$  are placed in a flask at  $397^\circ\text{C}$ . Calculate the total pressure of the system at equilibrium if the mole fraction of  $\text{NH}_3$  is found to be 0.21. The  $K_P$  for the reaction is  $4.31 \times 10^{-4}$ .

- 15.67 At  $1130^\circ\text{C}$  the equilibrium constant ( $K_c$ ) for the reaction



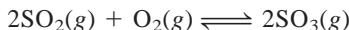
is  $2.25 \times 10^{-4}$ . If  $[\text{H}_2\text{S}] = 4.84 \times 10^{-3} \text{ M}$  and  $[\text{H}_2] = 1.50 \times 10^{-3} \text{ M}$ , calculate  $[\text{S}_2]$ .

- 15.68 A quantity of 6.75 g of  $\text{SO}_2\text{Cl}_2$  was placed in a 2.00-L flask. At 648 K, there is 0.0345 mole of  $\text{SO}_2$  present. Calculate  $K_c$  for the reaction



- 15.69 The formation of  $\text{SO}_3$  from  $\text{SO}_2$  and  $\text{O}_2$  is an intermediate step in the manufacture of sulfuric acid, and

it is also responsible for the acid rain phenomenon. The equilibrium constant ( $K_P$ ) for the reaction



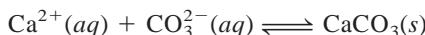
is 0.13 at 830°C. In one experiment 2.00 moles of  $\text{SO}_2$  and 2.00 moles of  $\text{O}_2$  were initially present in a flask. What must the total pressure be at equilibrium to have an 80.0 percent yield of  $\text{SO}_3$ ?

- 15.70** Consider the dissociation of iodine:



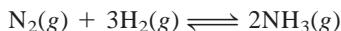
A 1.00-g sample of  $\text{I}_2$  is heated at 1200°C in a 500-mL flask. At equilibrium the total pressure is 1.51 atm. Calculate  $K_P$  for the reaction. [Hint: Use the result in problem 15.65(a). The degree of dissociation  $\alpha$  can be obtained by first calculating the ratio of observed pressure over calculated pressure, assuming no dissociation.]

- 15.71** Eggshells are composed mostly of calcium carbonate ( $\text{CaCO}_3$ ) formed by the reaction



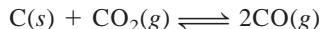
The carbonate ions are supplied by carbon dioxide produced as a result of metabolism. Explain why eggshells are thinner in the summer, when the rate of chicken panting is greater. Suggest a remedy for this situation.

- 15.72** The equilibrium constant  $K_P$  for the following reaction is found to be  $4.31 \times 10^{-4}$  at 375°C:



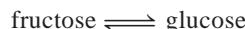
In a certain experiment a student starts with 0.862 atm of  $\text{N}_2$  and 0.373 atm of  $\text{H}_2$  in a constant-volume vessel at 375°C. Calculate the partial pressures of all species when equilibrium is reached.

- 15.73** A quantity of 0.20 mole of carbon dioxide was heated at a certain temperature with an excess of graphite in a closed container until the following equilibrium was reached:



Under this condition, the average molar mass of the gases was found to be 35 g/mol. (a) Calculate the mole fractions of CO and  $\text{CO}_2$ . (b) What is the  $K_P$  for the equilibrium if the total pressure was 11 atm? (Hint: The average molar mass is the sum of the products of the mole fraction of each gas and its molar mass.)

- 15.74** When dissolved in water, glucose (corn sugar) and fructose (fruit sugar) exist in equilibrium as follows:



A chemist prepared a 0.244 M fructose solution at 25°C. At equilibrium, it was found that its concentration had decreased to 0.113 M. (a) Calculate the equi-

librium constant for the reaction. (b) At equilibrium, what percentage of fructose was converted to glucose?

- 15.75** At room temperature, solid iodine is in equilibrium with its vapor through sublimation and deposition (see Figure 8.17). Describe how you would use radioactive iodine, in either solid or vapor form, to show that there is a dynamic equilibrium between these two phases.

- 15.76** At 1024°C, the pressure of oxygen gas from the decomposition of copper(II) oxide ( $\text{CuO}$ ) is 0.49 atm:



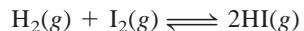
(a) What is the  $K_P$  for the reaction? (b) Calculate the fraction of  $\text{CuO}$  decomposed if 0.16 mole of it is placed in a 2.0-L flask at 1024°C. (c) What would be the fraction if a 1.0-mole sample of  $\text{CuO}$  were used? (d) What is the smallest amount of  $\text{CuO}$  (in moles) that would establish the equilibrium?

- 15.77** A mixture containing 3.9 moles of NO and 0.88 mole of  $\text{CO}_2$  was allowed to react in a flask at a certain temperature according to the equation



At equilibrium, 0.11 mole of  $\text{CO}_2$  was present. Calculate the equilibrium constant  $K_c$  of this reaction.

- 15.78** The equilibrium constant  $K_c$  for the reaction



is 54.3 at 430°C. At the start of the reaction there are 0.714 mole of  $\text{H}_2$ , 0.984 mole of  $\text{I}_2$ , and 0.886 mole of  $\text{HI}$  in a 2.40-L reaction chamber. Calculate the concentrations of the gases at equilibrium.

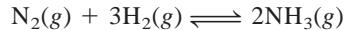
- 15.79** On heating, a gaseous compound A dissociates as follows:



In an experiment A was heated at a certain temperature until its equilibrium pressure reached  $0.14P$ , in which  $P$  is the total pressure. Calculate the equilibrium constant ( $K_P$ ) of this reaction.

- 15.80** When a gas was heated under atmospheric conditions, its color was found to deepen. Heating above 150°C caused the color to fade, and at 550°C the color was barely detectable. However, at 550°C, the color was partially restored by increasing the pressure of the system. Which of these best fits this description? Justify your choice. (a) A mixture of hydrogen and bromine, (b) pure bromine, (c) a mixture of nitrogen dioxide and dinitrogen tetroxide. (Hint: Bromine has a reddish color and nitrogen dioxide is a brown gas. The other gases are colorless.)

- 15.81** The equilibrium constant  $K_c$  for the following reaction is 0.65 at 395°C.



- (a) What is the value of  $K_P$  for this reaction?  
 (b) What is the value of the equilibrium constant  $K_c$  for  $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$ ?  
 (c) What is  $K_c$  for  $\frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{H}_2(g) \rightleftharpoons \text{NH}_3(g)$ ?  
 (d) What are the values of  $K_P$  for the reactions described in (b) and (c)?

- 15.82** A sealed glass bulb contains a mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  gases. When the bulb is heated from  $20^\circ\text{C}$  to  $40^\circ\text{C}$ , what happens to these properties of the gases: (a) color, (b) pressure, (c) average molar mass, (d) degree of dissociation (from  $\text{N}_2\text{O}_4$  to  $\text{NO}_2$ ), (e) density? Assume that volume remains constant. (*Hint:*  $\text{NO}_2$  is a brown gas;  $\text{N}_2\text{O}_4$  is colorless.)
- 15.83 At  $20^\circ\text{C}$ , the vapor pressure of water is 0.0231 atm. Calculate  $K_P$  and  $K_c$  for the process



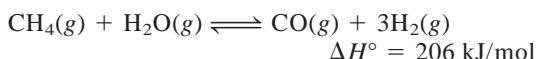
- 15.84** Industrially, sodium metal is obtained by electrolyzing molten sodium chloride. The reaction at the cathode is  $\text{Na}^+ + e^- \rightarrow \text{Na}$ . We might expect that potassium metal would also be prepared by electrolyzing molten potassium chloride. However, potassium metal is soluble in molten potassium chloride and therefore is hard to recover. Furthermore, potassium vaporizes readily at the operating temperature, creating hazardous conditions. Instead, potassium is prepared by the distillation of molten potassium chloride in the presence of sodium vapor at  $892^\circ\text{C}$ :



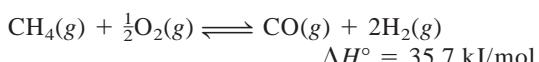
In view of the fact that potassium is a stronger reducing agent than sodium, explain why this approach works. (The boiling points of sodium and potassium are  $892^\circ\text{C}$  and  $770^\circ\text{C}$ , respectively.)

- 15.85 In the gas phase, nitrogen dioxide is actually a mixture of nitrogen dioxide ( $\text{NO}_2$ ) and dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ ). If the density of such a mixture at  $74^\circ\text{C}$  and 1.3 atm is 2.9 g/L, calculate the partial pressures of the gases and  $K_P$ .

- 15.86** About 75 percent of hydrogen for industrial use is produced by the *steam-reforming* process. This process is carried out in two stages called primary and secondary reforming. In the primary stage, a mixture of steam and methane at about 30 atm is heated over a nickel catalyst at  $800^\circ\text{C}$  to give hydrogen and carbon monoxide:

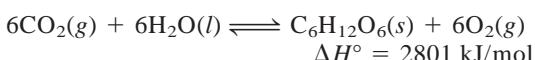


The secondary stage is carried out at about  $1000^\circ\text{C}$ , in the presence of air, to convert the remaining methane to hydrogen:



- (a) What conditions of temperature and pressure would favor the formation of products in both the primary and secondary stages? (b) The equilibrium constant  $K_c$  for the primary stage is 18 at  $800^\circ\text{C}$ . (i) Calculate  $K_P$  for the reaction. (ii) If the partial pressures of methane and steam were both 15 atm at the start, what are the pressures of all the gases at equilibrium?

- 15.87 Photosynthesis can be represented by



Explain how the equilibrium would be affected by the following changes: (a) partial pressure of  $\text{CO}_2$  is increased, (b)  $\text{O}_2$  is removed from the mixture, (c)  $\text{C}_6\text{H}_{12}\text{O}_6$  (sucrose) is removed from the mixture, (d) more water is added, (e) a catalyst is added, (f) temperature is decreased, (g) more sunlight falls on the plants.

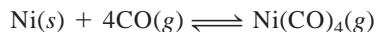
- 15.88** Consider the decomposition of ammonium chloride at a certain temperature:



Calculate the equilibrium constant  $K_P$  if the total pressure is 2.2 atm at that temperature.

- 15.89 At  $25^\circ\text{C}$ , the equilibrium partial pressures of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  are 0.15 atm and 0.20 atm, respectively. If the volume is doubled at constant temperature, calculate the partial pressures of the gases when a new equilibrium is established.

- 15.90** In 1899 the German chemist Ludwig Mond developed a process for purifying nickel by converting it to the volatile nickel tetracarbonyl  $[\text{Ni}(\text{CO})_4]$  (b.p. =  $42.2^\circ\text{C}$ ):



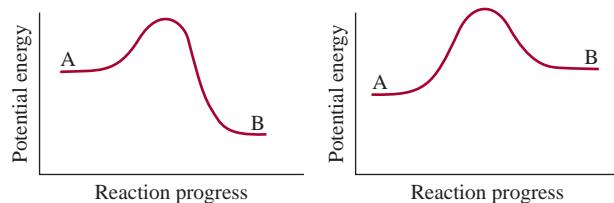
(a) Describe how you can separate nickel and its solid impurities. (b) How would you recover nickel? [ $\Delta H_f^\circ$  for  $\text{Ni}(\text{CO})_4$  is  $-602.9 \text{ kJ/mol}$ .]

- 15.91 Consider the equilibrium reaction in Problem 15.21. A quantity of 2.50 g of  $\text{PCl}_5$  is placed in an evacuated flask of volume 0.500 L and heated to  $250^\circ\text{C}$ . (a) Calculate the pressure of  $\text{PCl}_5$  if it did not dissociate. (b) Calculate the partial pressure of  $\text{PCl}_5$  at equilibrium. (c) What is the total pressure at equilibrium? (d) What is the degree of dissociation of  $\text{PCl}_5$ ? (The degree of dissociation is given by the fraction of  $\text{PCl}_5$  that has undergone dissociation.)

- 15.92** The vapor pressure of mercury is 0.0020 mmHg at  $26^\circ\text{C}$ . (a) Calculate  $K_c$  and  $K_P$  for the process  $\text{Hg}(l) \rightleftharpoons \text{Hg}(g)$ . (b) A chemist breaks a thermometer and spills mercury onto the floor of a laboratory measuring 6.1 m long, 5.3 m wide, and 3.1 m high. Calculate the mass of mercury (in grams) vaporized at equilibrium and the concentration of mercury

vapor in mg/m<sup>3</sup>. Does this concentration exceed the safety limit of 0.050 mg/m<sup>3</sup>? (Ignore the volume of furniture and other objects in the laboratory.)

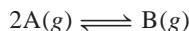
- 15.93 Consider the potential energy diagrams for two types of reactions A  $\rightleftharpoons$  B. In each case, answer the following questions for the system at equilibrium. (a) How would a catalyst affect the forward and reverse rates of the reaction? (b) How would a catalyst affect the energies of the reactant and product? (c) How would an increase in temperature affect the equilibrium constant? (d) If the only effect of a catalyst is to lower the activation energies for the forward and reverse reactions, show that the equilibrium constant remains unchanged if a catalyst is added to the reacting mixture.



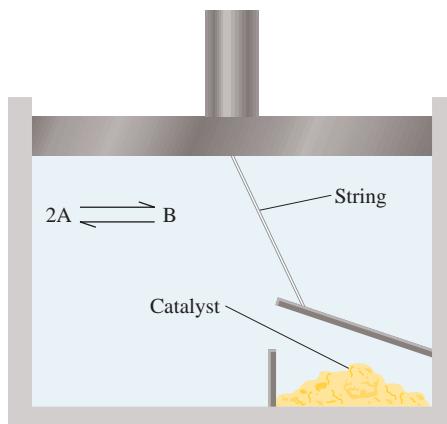
- 15.94 The equilibrium constant  $K_c$  for the reaction  $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$  is 0.83 at 375°C. A 14.6-g sample of ammonia is placed in a 4.00-L flask and heated to 375°C. Calculate the concentrations of all the gases when equilibrium is reached.

## SPECIAL PROBLEMS

- 15.95 In this chapter we learned that a catalyst has no effect on the position of an equilibrium because it speeds up both the forward and reverse rates to the same extent. To test this statement, consider a situation in which an equilibrium of the type



is established inside a cylinder fitted with a weightless piston. The piston is attached by a string to the cover of a box containing a catalyst. When the piston moves upward (expanding against atmospheric pressure), the cover is lifted and the catalyst is exposed to the gases. When the piston moves downward, the box is closed. Assume that the catalyst speeds up the forward reaction ( $2\text{A} \rightarrow \text{B}$ ) but does not affect the reverse process ( $\text{B} \rightarrow 2\text{A}$ ). Suppose the catalyst is suddenly exposed to the equilibrium system as shown below. Describe what would happen subsequently. How does this "thought" experiment convince you that no such catalyst can exist?

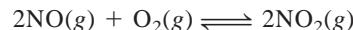


- 15.96 At 25°C, a mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  gases are in equilibrium in a cylinder fitted with a movable piston. The concentrations are:  $[\text{NO}_2] = 0.0475\text{ M}$  and  $[\text{N}_2\text{O}_4] = 0.491\text{ M}$ . The volume of the gas mixture is halved by pushing down on the piston at constant temperature. Calculate the concentrations of the gases when equilibrium is reestablished. Will the color become darker or lighter after the change? [Hint:  $K_c$  for the dissociation of  $\text{N}_2\text{O}_4$  is  $4.63 \times 10^{-3}$ .  $\text{N}_2\text{O}_4(g)$  is colorless and  $\text{NO}_2(g)$  has a brown color.]

- 15.97 The dependence of the equilibrium constant of a reaction on temperature is given by the van't Hoff equation:

$$\ln K = -\frac{\Delta H^\circ}{RT} + C$$

where  $C$  is a constant. The following table gives the equilibrium constant ( $K_P$ ) for the reaction at various temperatures



|               |     |      |       |        |        |
|---------------|-----|------|-------|--------|--------|
| $K_P$         | 138 | 5.12 | 0.436 | 0.0626 | 0.0130 |
| $T(\text{K})$ | 600 | 700  | 800   | 900    | 1000   |

Determine graphically the  $\Delta H^\circ$  for the reaction.

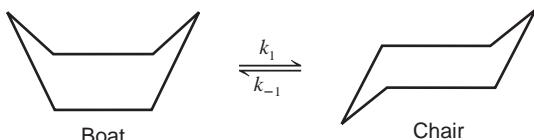
- 15.98 (a) Use the van't Hoff equation in Problem 15.97 to derive the following expression, which relates the equilibrium constants at two different temperatures

$$\ln \frac{K_1}{K_2} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

How does this equation support the prediction based on Le Châtelier's principle about the shift in equilibrium with temperature? (b) The vapor pressures of

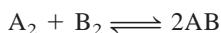
water are 31.82 mmHg at 30°C and 92.51 mmHg at 50°C. Calculate the molar heat of vaporization of water.

- 15.99** The “boat” form and “chair” form of cyclohexane ( $C_6H_{12}$ ) interconverts as shown here:



In this representation, the H atoms are omitted and a C atom is assumed to be at each intersection of two lines (bonds). The conversion is first order in each direction. The activation energy for the chair  $\rightarrow$  boat conversion is 41 kJ/mol. If the frequency factor is  $1.0 \times 10^{12} \text{ s}^{-1}$ , what is  $k_1$  at 298 K? The equilibrium constant  $K_c$  for the reaction is  $9.83 \times 10^3$  at 298 K.

- 15.100** Consider the following reaction at a certain temperature



The mixing of 1 mole of  $A_2$  with 3 moles of  $B_2$  gives rise to  $x$  mole of  $AB$  at equilibrium. The addition of 2 more moles of  $A_2$  produces another  $x$  mole of  $AB$ . What is the equilibrium constant for the reaction?

- 15.101** Iodine is sparingly soluble in water but much more so in carbon tetrachloride ( $CCl_4$ ). The equilibrium constant, also called the partition coefficient, for the distribution of  $I_2$  between these two phases



is 83 at 20°C. (a) A student adds 0.030 L of  $CCl_4$  to 0.200 L of an aqueous solution containing 0.032 g  $I_2$ . The mixture is shaken and the two phases are then allowed to separate. Calculate the fraction of  $I_2$  remaining in the aqueous phase. (b) The student now repeats the extraction of  $I_2$  with another 0.030 L of  $CCl_4$ . Calculate the fraction of the  $I_2$  from the original solution that remains in the aqueous phase. (c) Compare the result in (b) with a single extraction using 0.060 L of  $CCl_4$ . Comment on the difference.

## ANSWERS TO PRACTICE EXERCISES

**15.1**  $K_c = \frac{[NO_2]^4 [O_2]}{[N_2O_5]^2}$   $K_P = \frac{P_{NO_2}^4 P_{O_2}}{P_{N_2O_5}^2}$ .

- 15.2** 347 atm. **15.3** 1.2. **15.4**  $K_P = 0.0702$ ;  $K_c = 1.20 \times 10^{-4}$ . **15.5** From right to left. **15.6**  $[HI] = 0.031 M$ ,  $[H_2] = 4.3 \times 10^{-3} M$ ,  $[I_2] = 4.3 \times 10^{-3} M$ . **15.7**  $[Br_2] = 0.065 M$ ,

$[Br] = 8.4 \times 10^{-3} M$ . **15.8**  $Q_P = 4.0 \times 10^5$ , the net reaction will shift from right to left. **15.9** Left to right.

- 15.10** The equilibrium will shift from (a) left to right, (b) left to right, and (c) right to left. (d) A catalyst has no effect on the equilibrium.

Many organic acids occur in the vegetable kingdom. Lemons, oranges, and tomatoes contain ascorbic acid and citric acid and rhubarbs and spinach contain oxalic acid.



## Acids and Bases

### CHAPTER OUTLINE

- 16.1** Brønsted Acids and Bases 530  
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1. Animation: Acid Ionization (16.5)
2. Interactivity: Calculating pH of Acid Solution (16.5)
3. Animation: Base Ionization (16.6)

### ESSENTIAL CONCEPTS

**Brønsted Acids and Bases** A Brønsted acid can donate a proton and a Brønsted base can accept a proton. For every Brønsted acid, there exists a conjugate Brønsted base and vice versa.

**Acid-Base Properties of Water and the pH Scale** Water acts both as a Brønsted acid and as a Brønsted base. At 25°C, the concentrations of  $\text{H}^+$  and  $\text{OH}^-$  ions are both at  $10^{-7} \text{ M}$ . The pH scale is established to express the acidity of a solution—the smaller the pH, the higher the  $\text{H}^+$  concentration and the greater the acidity.

**Acid and Base Ionization Constants** Strong acids and strong bases are assumed to ionize completely. Most weak acids and bases ionize to a small extent. The concentrations of the acid, conjugate base, and  $\text{H}^+$  ion at equilibrium can be calculated from the acid ionization constant, which is the equilibrium constant for the reaction.

**Molecular Structure and Acid Strength** The strength of a series of structurally similar acids can be compared using parameters such as bond enthalpy, bond polarity, and oxidation number.

**Acid-Base Properties of Salts and Oxides** Many salts react with water in a process called hydrolysis. From the nature of the cation and anion present in the salt, it is possible to predict the pH of the resulting solution. Most oxides also react with water to produce acidic or basic solutions.

**Lewis Acids and Bases** A more general definition of acids and bases characterizes an acid as a substance that can accept a pair of electrons and a base as a substance that can donate a pair of electrons. All Brønsted acids and bases are Lewis acids and bases.

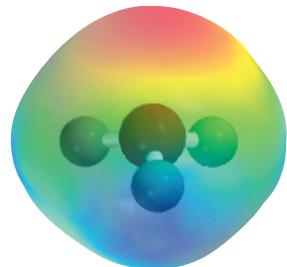
4. Interactivity: Calculating pH of Base Solution (16.6)
5. Interactivity: Molecular Structure and Acid Strength (16.8)
6. Interactivity: Acid-Base Properties of Salts (16.9)

## 16.1 Brønsted Acids and Bases

In Chapter 4 we defined a Brønsted acid as a substance capable of donating a proton, and a Brønsted base as a substance capable of accepting a proton. These definitions are generally suitable for discussion of the properties and reactions of acids and bases.

### Conjugate Acid-Base Pairs

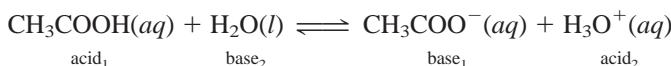
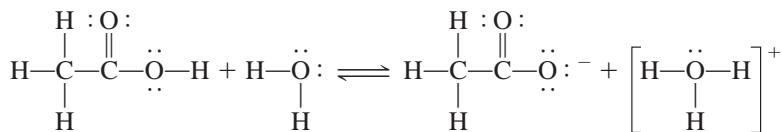
Conjugate means “joined together.”



Electrostatic potential map of the hydronium ion. The proton is always associated with water molecules in aqueous solution. The  $\text{H}_3\text{O}^+$  ion is the simplest formula of a hydrated proton.

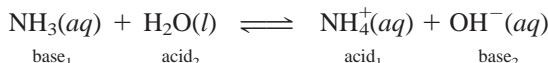
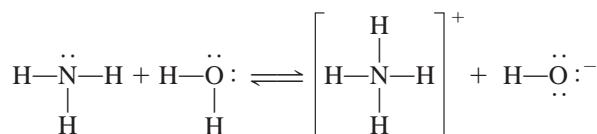
An extension of the Brønsted definition of acids and bases is the concept of the **conjugate acid-base pair**, which can be defined as *an acid and its conjugate base or a base and its conjugate acid*. The conjugate base of a Brønsted acid is the species that remains when one proton has been removed from the acid. Conversely, a conjugate acid results from the addition of a proton to a Brønsted base.

Every Brønsted acid has a conjugate base, and every Brønsted base has a conjugate acid. For example, the chloride ion ( $\text{Cl}^-$ ) is the conjugate base formed from the acid  $\text{HCl}$ , and  $\text{H}_2\text{O}$  is the conjugate base of the acid  $\text{H}_3\text{O}^+$ . Similarly, the ionization of acetic acid can be represented as



The subscripts 1 and 2 designate the two conjugate acid-base pairs. Thus, the acetate ion ( $\text{CH}_3\text{COO}^-$ ) is the conjugate base of the acid  $\text{CH}_3\text{COOH}$ . Both the ionization of  $\text{HCl}$  (see Section 4.3) and the ionization of  $\text{CH}_3\text{COOH}$  are examples of Brønsted acid-base reactions.

The Brønsted definition also enables us to classify ammonia as a base because of its ability to accept a proton:



In this case,  $\text{NH}_4^+$  is the conjugate acid of the base  $\text{NH}_3$ , and  $\text{OH}^-$  is the conjugate base of the acid  $\text{H}_2\text{O}$ . Note that the atom in the Brønsted base that accepts a  $\text{H}^+$  ion must have a lone pair.

### Example 16.1

Identify the conjugate acid-base pairs in the reaction between ammonia and hydrofluoric acid in aqueous solution



(Continued)

**Strategy** Remember that a conjugate base always has one fewer H atom and one more negative charge (or one fewer positive charge) than the formula of the corresponding acid.

**Solution** NH<sub>3</sub> has one fewer H atom and one fewer positive charge than NH<sub>4</sub><sup>+</sup>. F<sup>-</sup> has one fewer H atom and one more negative charge than HF. Therefore, the conjugate acid-base pairs are (1) NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub> and (2) HF and F<sup>-</sup>.

**Similar problem:** 16.5.

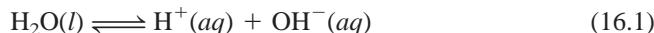
**Practice Exercise** Identify the conjugate acid-base pairs for the reaction



It is acceptable to represent the proton in aqueous solution either as H<sup>+</sup> or as H<sub>3</sub>O<sup>+</sup>. The formula H<sup>+</sup> is less cumbersome in calculations involving hydrogen ion concentrations and in calculations involving equilibrium constants, whereas H<sub>3</sub>O<sup>+</sup> is more representative of the proton in aqueous solution.

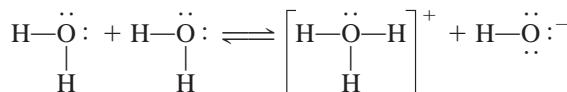
## 16.2 The Acid-Base Properties of Water

Water, as we know, is a unique solvent. One of its special properties is its ability to act either as an acid or as a base. Water functions as a base in reactions with acids such as HCl and CH<sub>3</sub>COOH, and it functions as an acid in reactions with bases such as NH<sub>3</sub>. Water is a very weak electrolyte and therefore a poor conductor of electricity, but it does undergo ionization to a small extent:

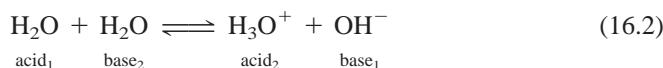


**Tap water and water from underground sources do conduct electricity because they contain many dissolved ions.**

This reaction is sometimes called the *autoionization* of water. To describe the acid-base properties of water in the Brønsted framework, we express its autoionization as follows (also shown in Figure 16.1):



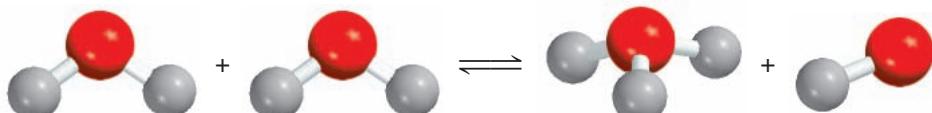
or



The acid-base conjugate pairs are (1) H<sub>2</sub>O (acid) and OH<sup>-</sup> (base) and (2) H<sub>3</sub>O<sup>+</sup> (acid) and H<sub>2</sub>O (base).

### The Ion Product of Water

In the study of acid-base reactions, the hydrogen ion concentration is key; its value indicates the acidity or basicity of the solution. Because only a very small fraction of



**Figure 16.1**  
Reaction between two water molecules to form hydronium and hydroxide ions.

Recall that in pure water,  $[H_2O] = 55.5\text{ M}$  (see p. 502).

water molecules are ionized, the concentration of water,  $[H_2O]$ , remains virtually unchanged. Therefore, the equilibrium constant for the autoionization of water, according to Equation (16.2), is

$$K_c = [H_3O^+][OH^-]$$

Because we use  $H^+(aq)$  and  $H_3O^+(aq)$  interchangeably to represent the hydrated proton, the equilibrium constant can also be expressed as

$$K_c = [H^+][OH^-]$$

To indicate that the equilibrium constant refers to the autoionization of water, we replace  $K_c$  by  $K_w$

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-] \quad (16.3)$$

where  $K_w$  is called the **ion-product constant**, which is *the product of the molar concentrations of  $H^+$  and  $OH^-$  ions at a particular temperature*.

In pure water at  $25^\circ\text{C}$ , the concentrations of  $H^+$  and  $OH^-$  ions are equal and found to be  $[H^+] = 1.0 \times 10^{-7}\text{ M}$  and  $[OH^-] = 1.0 \times 10^{-7}\text{ M}$ . Thus, from Equation (16.3), at  $25^\circ\text{C}$

$$K_w = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

Whether we have pure water or an aqueous solution of dissolved species, the following relation *always* holds at  $25^\circ\text{C}$ :

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \quad (16.4)$$

Whenever  $[H^+] = [OH^-]$  the aqueous solution is said to be neutral. In an acidic solution, there is an excess of  $H^+$  ions and  $[H^+] > [OH^-]$ . In a basic solution, there is an excess of hydroxide ions, so  $[H^+] < [OH^-]$ . In practice, we can change the concentration of either  $H^+$  or  $OH^-$  ions in solution, but we cannot vary both of them independently. If we adjust the solution so that  $[H^+] = 1.0 \times 10^{-6}\text{ M}$ , the  $OH^-$  concentration *must* change to

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-6}} = 1.0 \times 10^{-8}\text{ M}$$

### Example 16.2

The concentration of  $OH^-$  ions in a certain household ammonia cleaning solution is  $0.0025\text{ M}$ . Calculate the concentration of  $H^+$  ions.

**Strategy** We are given the concentration of the  $OH^-$  ions and asked to calculate  $[H^+]$ . The relationship between  $[H^+]$  and  $[OH^-]$  in water or an aqueous solution is given by the ion-product of water,  $K_w$  [Equation (16.4)].

**Solution** Rearranging Equation (16.4), we write

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.0025} = 4.0 \times 10^{-12}\text{ M}$$

(Continued)

**Check** Because  $[H^+] < [OH^-]$ , the solution is basic, as we would expect from the earlier discussion of the reaction of ammonia with water.

Similar problem: 16.16(c).

**Practice Exercise** Calculate the concentration of  $OH^-$  ions in a HCl solution whose hydrogen ion concentration is 1.3 M.

## 16.3 pH—A Measure of Acidity

Because the concentrations of  $H^+$  and  $OH^-$  ions in aqueous solutions are frequently very small numbers and therefore inconvenient to work with, the Danish chemist Soren Sorensen in 1909 proposed a more practical measure called pH. The **pH** of a solution is defined as *the negative logarithm of the hydrogen ion concentration (in mol/L)*:

$$pH = -\log[H_3O^+] \quad \text{or} \quad pH = -\log[H^+] \quad (16.5)$$

Note that a unit pH change corresponds to a 10-fold change in  $[H^+]$ .

Keep in mind that Equation (16.5) is simply a definition designed to give us convenient numbers to work with. The negative logarithm gives us a positive number for pH, which otherwise would be negative due to the small value of  $[H^+]$ . Furthermore, the term  $[H^+]$  in Equation (16.5) pertains only to the *numerical part* of the expression for hydrogen ion concentration, for we cannot take the logarithm of units. Thus, like the equilibrium constant, the pH of a solution is a dimensionless quantity.

Because pH is simply a way to express hydrogen ion concentration, acidic and basic solutions at 25°C can be distinguished by their pH values, as follows:

|                    |  |
|--------------------|--|
| Acidic solutions:  | $[H^+] > 1.0 \times 10^{-7} M$ , pH < 7.00 |
| Basic solutions:   | $[H^+] < 1.0 \times 10^{-7} M$ , pH > 7.00 |
| Neutral solutions: | $[H^+] = 1.0 \times 10^{-7} M$ , pH = 7.00 |

The pH of concentrated acid solutions can be negative. For example, the pH of a 2.0 M HCl solution is -0.30.

Notice that pH increases as  $[H^+]$  decreases.

Sometimes we may be given the pH value of a solution and asked to calculate the  $H^+$  ion concentration. In that case, we need to take the antilog of Equation (16.5) as follows:

$$[H^+] = 10^{-pH} \quad (16.6)$$

Be aware that the definition of pH just shown, and indeed all the calculations involving solution concentrations (expressed either as molarity or molality) discussed in previous chapters, are subject to error because we have implicitly assumed ideal behavior. In reality, ion-pair formation and other types of intermolecular interactions may affect the actual concentrations of species in solution. The situation is analogous to the relationships between ideal gas behavior and the behavior of real gases discussed in Chapter 5. Depending on temperature, volume, and amount and type of gas present, the measured gas pressure may differ from that calculated using the ideal gas equation. Similarly, the actual or “effective” concentration of a solute may not be what we think it is, knowing the amount of substance originally dissolved in solution. Just as we have the van der Waals and other equations to reconcile discrepancies between the ideal gas and nonideal gas behavior, we can account for nonideal behavior in solution.

One way is to replace the concentration term with *activity*, which is the effective concentration. Strictly speaking, then, the pH of solution should be defined as

$$pH = -\log a_{H^+} \quad (16.7)$$

**Figure 16.2**

A pH meter is commonly used in the laboratory to determine the pH of a solution. Although many pH meters have scales marked with values from 1 to 14, pH values can, in fact, be less than 1 and greater than 14.



In dilute solutions, molarity is numerically equal to activity.

where  $a_{H^+}$  is the activity of the  $H^+$  ion. As mentioned in Chapter 15 (see p. 502), for an ideal solution activity is numerically equal to concentration. For real solutions, activity usually differs from concentration, sometimes appreciably. Knowing the solute concentration, there are reliable ways based on thermodynamics for estimating its activity, but the details are beyond the scope of this text. Keep in mind, therefore, that the measured pH of a solution is usually not the same as that calculated from Equation (16.5) because the concentration of the  $H^+$  ion in molarity is not numerically equal to its activity value. Although we will continue to use concentration in our discussion, it is important to know that this approach will give us only an approximation of the chemical processes that actually take place in the solution phase.

In the laboratory, the pH of a solution is measured with a pH meter (Figure 16.2). Table 16.1 lists the pHs of a number of common fluids. As you can see, the pH of body fluids varies greatly, depending on location and function. The low pH (high acidity) of gastric juices facilitates digestion whereas a higher pH of blood is necessary for the transport of oxygen.

A pOH scale analogous to the pH scale can be devised using the negative logarithm of the hydroxide ion concentration of a solution. Thus, we define pOH as

$$pOH = -\log[OH^-] \quad (16.8)$$

Now consider again the ion-product constant for water at 25°C:

$$[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$$

Taking the negative logarithm of both sides, we obtain

$$\begin{aligned} -(\log[H^+] + \log[OH^-]) &= -\log(1.0 \times 10^{-14}) \\ -\log[H^+] - \log[OH^-] &= 14.00 \end{aligned}$$

From the definitions of pH and pOH we obtain

$$pH + pOH = 14.00 \quad (16.9)$$

\*Water exposed to air for a long period of time absorbs atmospheric  $CO_2$  to form carbonic acid,  $H_2CO_3$ .

Equation (16.9) provides us with another way to express the relationship between the  $H^+$  ion concentration and the  $OH^-$  ion concentration.

**TABLE 16.1**

### The pHs of Some Common Fluids

| Sample                       | pH Value  |
|------------------------------|-----------|
| Gastric juice in the stomach | 1.0–2.0   |
| Lemon juice                  | 2.4       |
| Vinegar                      | 3.0       |
| Grapefruit juice             | 3.2       |
| Orange juice                 | 3.5       |
| Urine                        | 4.8–7.5   |
| Water exposed to air*        | 5.5       |
| Saliva                       | 6.4–6.9   |
| Milk                         | 6.5       |
| Pure water                   | 7.0       |
| Blood                        | 7.35–7.45 |
| Tears                        | 7.4       |
| Milk of magnesia             | 10.6      |
| Household ammonia            | 11.5      |

### Example 16.3

The concentration of  $\text{H}^+$  ions in a bottle of table wine was  $3.2 \times 10^{-4} M$  right after the cork was removed. Only half of the wine was consumed. The other half, after it had been standing open to the air for a month, was found to have a hydrogen ion concentration equal to  $1.0 \times 10^{-3} M$ . Calculate the pH of the wine on these two occasions.

**Strategy** We are given the  $\text{H}^+$  ion concentration and asked to calculate the pH of the solution. What is the definition of pH?

**Solution** According to Equation (16.5),  $\text{pH} = -\log[\text{H}^+]$ . When the bottle was first opened,  $[\text{H}^+] = 3.2 \times 10^{-4} M$ , which we substitute in Equation (16.5)

$$\begin{aligned}\text{pH} &= -\log[\text{H}^+] \\ &= -\log(3.2 \times 10^{-4}) = 3.49\end{aligned}$$

On the second occasion,  $[\text{H}^+] = 1.0 \times 10^{-3} M$ , so that

$$\text{pH} = -\log(1.0 \times 10^{-3}) = 3.00$$

**Comment** The increase in hydrogen ion concentration (or decrease in pH) is largely the result of the conversion of some of the alcohol (ethanol) to acetic acid, a reaction that takes place in the presence of molecular oxygen.

**Practice Exercise** Nitric acid ( $\text{HNO}_3$ ) is used in the production of fertilizer, dyes, drugs, and explosives. Calculate the pH of a  $\text{HNO}_3$  solution having a hydrogen ion concentration of  $0.76 M$ .

In each case the pH has only two significant figures. The two digits to the right of the decimal in 3.49 tell us that there are two significant figures in the original number (see Appendix 3).

Similar problems: 16.17(a), (d).

### Example 16.4

The pH of rainwater collected in a certain region of the northeastern United States on a particular day was 4.82. Calculate the  $\text{H}^+$  ion concentration of the rainwater.

**Strategy** Here we are given the pH of a solution and asked to calculate  $[\text{H}^+]$ . Because pH is defined as  $\text{pH} = -\log[\text{H}^+]$ , we can solve for  $[\text{H}^+]$  by taking the antilog of the pH; that is,  $[\text{H}^+] = 10^{-\text{pH}}$ , as shown in Equation (16.6).

**Solution** From Equation (16.5)

$$\text{pH} = -\log[\text{H}^+] = 4.82$$

Therefore,

$$\log[\text{H}^+] = -4.82$$

To calculate  $[\text{H}^+]$ , we need to take the antilog of  $-4.82$

$$[\text{H}^+] = 10^{-4.82} = 1.5 \times 10^{-5} M$$

**Check** Because the pH is between 4 and 5, we can expect  $[\text{H}^+]$  to be between  $1 \times 10^{-4} M$  and  $1 \times 10^{-5} M$ . Therefore, the answer is reasonable.

**Practice Exercise** The pH of a certain orange juice is 3.33. Calculate the  $\text{H}^+$  ion concentration.

Scientific calculators have an antilog function that is sometimes labeled INV log or  $10^x$ .

Similar problems: 16.16(a), (b).

### Example 16.5

In a NaOH solution  $[\text{OH}^-]$  is  $2.9 \times 10^{-4} M$ . Calculate the pH of the solution.

**Strategy** Solving this problem takes two steps. First, we need to calculate pOH using Equation (16.8). Next, we use Equation (16.9) to calculate the pH of the solution.

**Solution** We use Equation (16.8):

$$\begin{aligned}\text{pOH} &= -\log[\text{OH}^-] \\ &= -\log(2.9 \times 10^{-4}) \\ &= 3.54\end{aligned}$$

Now we use Equation (16.9)

$$\begin{aligned}\text{pH} + \text{pOH} &= 14.00 \\ \text{pH} &= 14.00 - \text{pOH} \\ &= 14.00 - 3.54 = 10.46\end{aligned}$$

Alternatively, we can use the ion-product constant of water,  $K_w = [\text{H}^+][\text{OH}^-]$  to calculate  $[\text{H}^+]$ , and then we can calculate the pH from the  $[\text{H}^+]$ . Try it.

**Similar problem:** 16.17(b).

**Check** The answer shows that the solution is basic ( $\text{pH} > 7$ ), which is consistent with a NaOH solution.

**Practice Exercise** The  $\text{OH}^-$  ion concentration of a blood sample is  $2.5 \times 10^{-7} M$ . What is the pH of the blood?

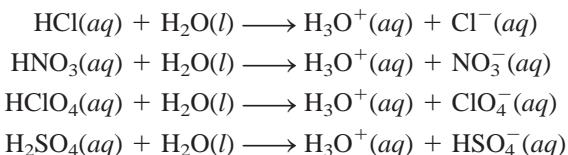
**In reality, no acids are known to ionize completely in water.**



Zn reacts more vigorously with a strong acid like HCl (left) than with a weak acid like  $\text{CH}_3\text{COOH}$  (right) of the same concentration because there are more  $\text{H}^+$  ions in the former solution.

## 16.4 Strength of Acids and Bases

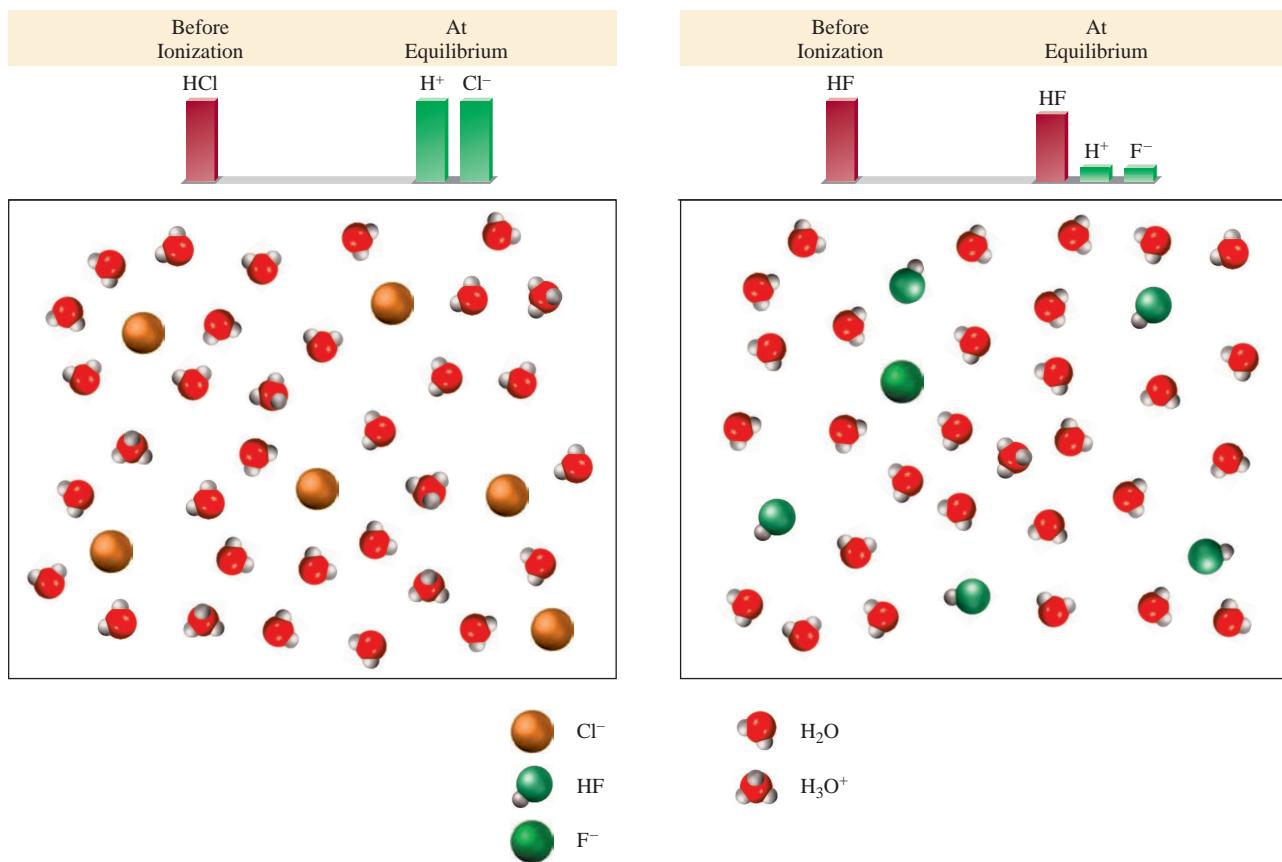
**Strong acids** are strong electrolytes which, for practical purposes, are assumed to ionize completely in water (Figure 16.3). Most of the strong acids are inorganic acids: hydrochloric acid (HCl), nitric acid ( $\text{HNO}_3$ ), perchloric acid ( $\text{HClO}_4$ ), and sulfuric acid ( $\text{H}_2\text{SO}_4$ ):



Note that  $\text{H}_2\text{SO}_4$  is a diprotic acid; we show only the first stage of ionization here. At equilibrium, solutions of strong acids will not contain any nonionized acid molecules.

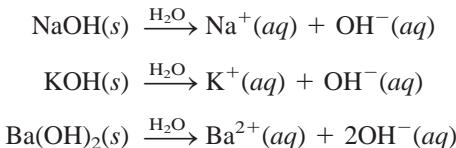
Most acids are **weak acids**, which ionize only to a limited extent in water. At equilibrium, aqueous solutions of weak acids contain a mixture of nonionized acid molecules,  $\text{H}_3\text{O}^+$  ions, and the conjugate base. Examples of weak acids are hydrofluoric acid (HF), acetic acid ( $\text{CH}_3\text{COOH}$ ), and the ammonium ion ( $\text{NH}_4^+$ ). The limited ionization of weak acids is related to the equilibrium constant for ionization, which we will study in the next section.

Like strong acids, **strong bases** are all strong electrolytes that ionize completely in water. Hydroxides of alkali metals and certain alkaline earth metals are strong bases. [All alkali metal hydroxides are soluble. Of the alkaline earth hydroxides,

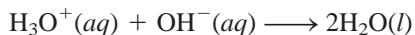
**Figure 16.3**

The extent of ionization of a strong acid such as HCl (left) and a weak acid such as HF (right). Initially, there were 6 HCl and 6 HF molecules present. The strong acid is assumed to be completely ionized in solution. The proton exists in solution as the hydronium ion ( $\text{H}_3\text{O}^+$ ).

Be(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> are insoluble; Ca(OH)<sub>2</sub> and Sr(OH)<sub>2</sub> are slightly soluble; and Ba(OH)<sub>2</sub> is soluble.] Some examples of strong bases are

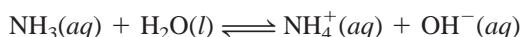


Strictly speaking, these metal hydroxides are not Brønsted bases because they cannot accept a proton. However, the hydroxide ion ( $\text{OH}^-$ ) formed when they ionize is a Brønsted base because it can accept a proton:



Thus, when we call NaOH or any other metal hydroxide a base, we are actually referring to the  $\text{OH}^-$  species derived from the hydroxide.

**Weak bases**, like weak acids, are weak electrolytes. Ammonia ionizes in water as follows:



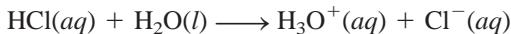
**TABLE 16.2** Relative Strengths of Conjugate Acid-Base Pairs

|  | Acid   | Conjugate Base                                       |
|--|--|--|
| Strong acids<br>↑<br>Acid strength increases | HClO <sub>4</sub> (perchloric acid)                  | ClO <sub>4</sub> <sup>-</sup> (perchlorate ion)      |
|  | HI (hydroiodic acid)                                 | I <sup>-</sup> (iodide ion)                          |
|  | HBr (hydrobromic acid)                               | Br <sup>-</sup> (bromide ion)                        |
|  | HCl (hydrochloric acid)                              | Cl <sup>-</sup> (chloride ion)                       |
|  | H <sub>2</sub> SO <sub>4</sub> (sulfuric acid)       | HSO <sub>4</sub> <sup>-</sup> (hydrogen sulfate ion) |
|  | HNO <sub>3</sub> (nitric acid)                       | NO <sub>3</sub> <sup>-</sup> (nitrate ion)           |
|  | H <sub>3</sub> O <sup>+</sup> (hydronium ion)        | H <sub>2</sub> O (water)                             |
|  | HSO <sub>4</sub> <sup>-</sup> (hydrogen sulfate ion) | SO <sub>4</sub> <sup>2-</sup> (sulfate ion)          |
|  | HF (hydrofluoric acid)                               | F <sup>-</sup> (fluoride ion)                        |
|  | HNO <sub>2</sub> (nitrous acid)                      | NO <sub>2</sub> <sup>-</sup> (nitrite ion)           |
| Weak acids<br>↓<br>Acid strength decreases   | HCOOH (formic acid)                                  | HCOO <sup>-</sup> (formate ion)                      |
|  | CH <sub>3</sub> COOH (acetic acid)                   | CH <sub>3</sub> COO <sup>-</sup> (acetate ion)       |
|  | NH <sub>4</sub> <sup>+</sup> (ammonium ion)          | NH <sub>3</sub> (ammonia)                            |
|  | HCN (hydrocyanic acid)                               | CN <sup>-</sup> (cyanide ion)                        |
|  | H <sub>2</sub> O (water)                             | OH <sup>-</sup> (hydroxide ion)                      |
|  | NH <sub>3</sub> (ammonia)                            | NH <sub>2</sub> <sup>-</sup> (amide ion)             |
|  |  |  |
|  |  |  |
|  |  | ↓<br>Base strength increases                         |

In this reaction, NH<sub>3</sub> acts as a base by accepting a proton from water to form NH<sub>4</sub><sup>+</sup> and OH<sup>-</sup> ions. It is a weak base because only a small fraction of the molecules undergo this reaction.

Table 16.2 lists some important conjugate acid-base pairs, in order of their relative strengths. Conjugate acid-base pairs have the following properties:

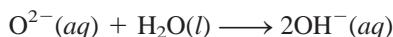
- If an acid is strong, its conjugate base has no measurable strength. Thus the Cl<sup>-</sup> ion, which is the conjugate base of the strong acid HCl, is an extremely weak base.
- H<sub>3</sub>O<sup>+</sup> is the strongest acid that can exist in aqueous solution. Acids stronger than H<sub>3</sub>O<sup>+</sup> react with water to produce H<sub>3</sub>O<sup>+</sup> and their conjugate bases. Thus HCl, which is a stronger acid than H<sub>3</sub>O<sup>+</sup>, reacts with water completely to form H<sub>3</sub>O<sup>+</sup> and Cl<sup>-</sup>:



Acids weaker than H<sub>3</sub>O<sup>+</sup> react with water to a much smaller extent, producing H<sub>3</sub>O<sup>+</sup> and their conjugate bases. For example, the following equilibrium lies largely to the left:



- The OH<sup>-</sup> ion is the strongest base that can exist in aqueous solution. Bases stronger than OH<sup>-</sup> react with water to produce OH<sup>-</sup> and their conjugate acids. For example, the oxide ion (O<sup>2-</sup>) is a stronger base than OH<sup>-</sup>, so it reacts with water completely as follows:



For this reason the oxide ion does not exist in aqueous solutions.

### Example 16.6

Calculate the pH of (a) a  $1.0 \times 10^{-3} M$  HCl solution and (b) a  $0.020 M$  Ba(OH)<sub>2</sub> solution.

**Strategy** Keep in mind that HCl is a strong acid and Ba(OH)<sub>2</sub> is a strong base. Thus, these species are completely ionized and no HCl or Ba(OH)<sub>2</sub> will be left in solution.

**Solution** (a) The ionization of HCl is



The concentrations of all the species (HCl, H<sup>+</sup>, and Cl<sup>-</sup>) before and after ionization can be represented as follows:

|              |                       |   |                       |   |                       |
|--------------|-----------------------|---|-----------------------|---|-----------------------|
|              | HCl(aq)               | → | H <sup>+</sup> (aq)   | + | Cl <sup>-</sup> (aq)  |
| Initial (M): | $1.0 \times 10^{-3}$  |   | 0.0                   |   | 0.0                   |
| Change (M):  | $-1.0 \times 10^{-3}$ |   | $+1.0 \times 10^{-3}$ |   | $+1.0 \times 10^{-3}$ |
| Final (M):   | 0.0                   |   | $1.0 \times 10^{-3}$  |   | $1.0 \times 10^{-3}$  |

A positive (+) change represents an increase and a negative (−) change indicates a decrease in concentration. Thus,

$$\begin{aligned} [\text{H}^+] &= 1.0 \times 10^{-3} M \\ \text{pH} &= -\log(1.0 \times 10^{-3}) \\ &= 3.00 \end{aligned}$$

(b) Ba(OH)<sub>2</sub> is a strong base; each Ba(OH)<sub>2</sub> unit produces two OH<sup>-</sup> ions:



The changes in the concentrations of all the species can be represented as follows:

|              |                          |   |                       |   |                       |
|--------------|--------------------------|---|-----------------------|---|-----------------------|
|              | Ba(OH) <sub>2</sub> (aq) | → | Ba <sup>2+</sup> (aq) | + | 2OH <sup>-</sup> (aq) |
| Initial (M): | 0.020                    |   | 0.00                  |   | 0.00                  |
| Change (M):  | $-0.020$                 |   | $+0.020$              |   | $+2(0.020)$           |
| Final (M):   | 0.00                     |   | 0.020                 |   | 0.040                 |

Thus,

$$\begin{aligned} [\text{OH}^-] &= 0.040 M \\ \text{pOH} &= -\log 0.040 = 1.40 \end{aligned}$$

Therefore, from Equation (16.9)

$$\begin{aligned} \text{pH} &= 14.00 - \text{pOH} \\ &= 14.00 - 1.40 \\ &= 12.60 \end{aligned}$$

**Check** Note that in both (a) and (b) we have neglected the contribution of the autoionization of water to [H<sup>+</sup>] and [OH<sup>-</sup>] because  $1.0 \times 10^{-7} M$  is so small compared with  $1.0 \times 10^{-3} M$  and  $0.040 M$ .

**Similar problems:** 16.17(a), (c).

**Practice Exercise** Calculate the pH of a  $1.8 \times 10^{-2} M$  Ba(OH)<sub>2</sub> solution.

### Example 16.7

Predict the direction of the following reaction in aqueous solution:



**Strategy** The problem is to determine whether, at equilibrium, the reaction will be shifted to the right, favoring HCN and  $\text{NO}_2^-$ , or to the left, favoring  $\text{HNO}_2$  and  $\text{CN}^-$ . Which of the two is a stronger acid and hence a stronger proton donor:  $\text{HNO}_2$  or HCN? Which of the two is a stronger base and hence a stronger proton acceptor:  $\text{CN}^-$  or  $\text{NO}_2^-$ ? Remember that the stronger the acid, the weaker its conjugate base.

**Solution** In Table 16.2 we see that  $\text{HNO}_2$  is a stronger acid than HCN. Thus,  $\text{CN}^-$  is a stronger base than  $\text{NO}_2^-$ . The net reaction will proceed from left to right as written because  $\text{HNO}_2$  is a better proton donor than HCN (and  $\text{CN}^-$  is a better proton acceptor than  $\text{NO}_2^-$ ).

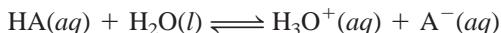
Similar problems: 16.35, 16.36.

**Practice Exercise** Predict whether the equilibrium constant for the following reaction is greater than or smaller than 1:



## 16.5 Weak Acids and Acid Ionization Constants

As we have seen, there are relatively few strong acids. The vast majority of acids are weak acids. Consider a weak monoprotic acid, HA. Its ionization in water is represented by



or simply



The equilibrium expression for this ionization is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad \text{or} \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (16.10)$$

where  $K_a$ , the **acid ionization constant**, is the *equilibrium constant for the ionization of an acid*. At a given temperature, the strength of the acid HA is measured quantitatively by the magnitude of  $K_a$ . The larger  $K_a$ , the stronger the acid—that is, the greater the concentration of  $\text{H}^+$  ions at equilibrium due to its ionization. Keep in mind, however, that only weak acids have  $K_a$  values associated with them.

Table 16.3 lists a number of weak acids and their  $K_a$  values at 25°C in order of decreasing acid strength. Although all these acids are weak, within the group there is great variation in their strengths. For example,  $K_a$  for HF ( $7.1 \times 10^{-4}$ ) is about 1.5 million times that for HCN ( $4.9 \times 10^{-10}$ ).

Generally, we can calculate the hydrogen ion concentration or pH of an acid solution at equilibrium, given the initial concentration of the acid and its  $K_a$  value. Alternatively, if we know the pH of a weak acid solution and its initial concentration, we can determine its  $K_a$ . The basic approach for solving these problems, which deal with

The back endpaper gives an index to all the useful tables and figures in the text.

**TABLE 16.3** Ionization Constants of Some Weak Acids and Their Conjugate Bases at 25°C

| Name of Acid                      | Formula                           | Structure                             | $K_a$                 | Conjugate Base                     | $K_b$                 |
|-----------------------------------|-----------------------------------|---------------------------------------|-----------------------|------------------------------------|-----------------------|
| Hydrofluoric acid                 | HF                                | H—F                                   | $7.1 \times 10^{-4}$  | $\text{F}^-$                       | $1.4 \times 10^{-11}$ |
| Nitrous acid                      | $\text{HNO}_2$                    | $\text{O}=\text{N}-\text{O}-\text{H}$ | $4.5 \times 10^{-4}$  | $\text{NO}_2^-$                    | $2.2 \times 10^{-11}$ |
| Acetylsalicylic acid<br>(aspirin) | $\text{C}_9\text{H}_8\text{O}_4$  |                                       | $3.0 \times 10^{-4}$  | $\text{C}_9\text{H}_7\text{O}_4^-$ | $3.3 \times 10^{-11}$ |
| Formic acid                       | $\text{HCOOH}$                    |                                       | $1.7 \times 10^{-4}$  | $\text{HCOO}^-$                    | $5.9 \times 10^{-11}$ |
| Ascorbic acid*                    | $\text{C}_6\text{H}_8\text{O}_6$  |                                       | $8.0 \times 10^{-5}$  | $\text{C}_6\text{H}_7\text{O}_6^-$ | $1.3 \times 10^{-10}$ |
| Benzoic acid                      | $\text{C}_6\text{H}_5\text{COOH}$ |                                       | $6.5 \times 10^{-5}$  | $\text{C}_6\text{H}_5\text{COO}^-$ | $1.5 \times 10^{-10}$ |
| Acetic acid                       | $\text{CH}_3\text{COOH}$          |                                       | $1.8 \times 10^{-5}$  | $\text{CH}_3\text{COO}^-$          | $5.6 \times 10^{-10}$ |
| Hydrocyanic acid                  | HCN                               | $\text{H}-\text{C}\equiv\text{N}$     | $4.9 \times 10^{-10}$ | $\text{CN}^-$                      | $2.0 \times 10^{-5}$  |
| Phenol                            | $\text{C}_6\text{H}_5\text{OH}$   |                                       | $1.3 \times 10^{-10}$ | $\text{C}_6\text{H}_5\text{O}^-$   | $7.7 \times 10^{-5}$  |

\*For ascorbic acid it is the upper left hydroxyl group that is associated with this ionization constant.

equilibrium concentrations, is the same one outlined in Chapter 15. However, because acid ionization represents a major category of chemical equilibrium in aqueous solution, we will develop a systematic procedure for solving this type of problem that will also help us to understand the chemistry involved.

Suppose we are asked to calculate the pH of a 0.50 M HF solution at 25°C. The ionization of HF is given by



From Table 16.3 we write

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = 7.1 \times 10^{-4}$$

The first step is to identify all the species present in solution that may affect its pH. Because weak acids ionize to a small extent, at equilibrium the major species present are nonionized HF and some  $\text{H}^+$  and  $\text{F}^-$  ions. Another major species is  $\text{H}_2\text{O}$ , but its very small  $K_w$  ( $1.0 \times 10^{-14}$ ) means that water is not a significant contributor to the  $\text{H}^+$  ion concentration. Therefore, unless otherwise stated, we will always ignore the  $\text{H}^+$  ions produced by the autoionization of water. Note that we need not be



**Interactivity:**  
Calculating pH of Acid  
Solution—Steps 1–4  
ARIS, Interactives

concerned with the  $\text{OH}^-$  ions that are also present in solution. The  $\text{OH}^-$  concentration can be determined from Equation (16.4) after we have calculated  $[\text{H}^+]$ .

We can summarize the changes in the concentrations of HF,  $\text{H}^+$ , and  $\text{F}^-$  according to the ICE method shown on p. 510 as follows:

|                      | $\text{HF}(aq)$ | $\rightleftharpoons$ | $\text{H}^+(aq) + \text{F}^-(aq)$ |
|----------------------|-----------------|----------------------|-----------------------------------|
| Initial ( $M$ ):     | 0.50            | 0.00                 | 0.00                              |
| Change ( $M$ ):      | $-x$            | $+x$                 | $+x$                              |
| Equilibrium ( $M$ ): | $0.50 - x$      | $x$                  | $x$                               |

The equilibrium concentrations of HF,  $\text{H}^+$ , and  $\text{F}^-$ , expressed in terms of the unknown  $x$ , are substituted into the ionization constant expression to give

$$K_a = \frac{(x)(x)}{0.50 - x} = 7.1 \times 10^{-4}$$

Rearranging this expression, we write

$$x^2 + 7.1 \times 10^{-4}x - 3.6 \times 10^{-4} = 0$$

This is a quadratic equation, which can be solved using the quadratic formula (see Appendix 3). Or we can try using a shortcut to solve for  $x$ . Because HF is a weak acid and weak acids ionize only to a slight extent, we reason that  $x$  must be small compared to 0.50. Therefore, we can make the approximation

$$0.50 - x \approx 0.50$$

Now the ionization constant expression becomes

$$\frac{x^2}{0.50 - x} \approx \frac{x^2}{0.50} = 7.1 \times 10^{-4}$$

Rearranging, we get

$$\begin{aligned} x^2 &= (0.50)(7.1 \times 10^{-4}) = 3.55 \times 10^{-4} \\ x &= \sqrt{3.55 \times 10^{-4}} = 0.019 \text{ M} \end{aligned}$$

Thus, we have solved for  $x$  without having to use the quadratic equation. At equilibrium, we have

$$\begin{aligned} [\text{HF}] &= (0.50 - 0.019) \text{ M} = 0.48 \text{ M} \\ [\text{H}^+] &= 0.019 \text{ M} \\ [\text{F}^-] &= 0.019 \text{ M} \end{aligned}$$

and the pH of the solution is

$$\text{pH} = -\log(0.019) = 1.72$$

How good is this approximation? Because  $K_a$  values for weak acids are generally known to an accuracy of only  $\pm 5\%$ , it is reasonable to require  $x$  to be less than 5% of 0.50, the number from which it is subtracted. In other words, the approximation is valid if the following expression is equal to or less than 5%:

$$\frac{0.019 \text{ M}}{0.50 \text{ M}} \times 100\% = 3.8\%$$

Thus, the approximation we made is acceptable.

The sign  $\approx$  means "approximately equal to." An analogy of the approximation is a truck loaded with coal. Losing a few lumps of coal on a delivery trip will not appreciably change the overall mass of the load.

Now consider a different situation. If the initial concentration of HF is 0.050 M, and we use the above procedure to solve for  $x$ , we would get  $6.0 \times 10^{-3}$  M. However, the following test shows that this answer is not a valid approximation because it is greater than 5% of 0.050 M:

$$\frac{6.0 \times 10^{-3} \text{ M}}{0.050 \text{ M}} \times 100\% = 12\%$$

In this case, we can solve for  $x$  by using the quadratic equation.

We start by writing the ionization expression in terms of the unknown  $x$ :

$$\frac{x^2}{0.050 - x} = 7.1 \times 10^{-4}$$

$$x^2 + 7.1 \times 10^{-4}x - 3.6 \times 10^{-5} = 0$$

This expression fits the quadratic equation  $ax^2 + bx + c = 0$ . Using the quadratic formula, we write

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-7.1 \times 10^{-4} \pm \sqrt{(7.1 \times 10^{-4})^2 - 4(1)(-3.6 \times 10^{-5})}}{2(1)}$$

$$= \frac{-7.1 \times 10^{-4} \pm 0.012}{2}$$

$$= 5.6 \times 10^{-3} \text{ M} \quad \text{or} \quad -6.4 \times 10^{-3} \text{ M}$$

The second solution ( $x = -6.4 \times 10^{-3}$  M) is physically impossible because the concentration of ions produced as a result of ionization cannot be negative. Choosing  $x = 5.6 \times 10^{-3}$  M, we can solve for [HF],  $[\text{H}^+]$ , and  $[\text{F}^-]$  as follows:

$$[\text{HF}] = (0.050 - 5.6 \times 10^{-3}) \text{ M} = 0.044 \text{ M}$$

$$[\text{H}^+] = 5.6 \times 10^{-3} \text{ M}$$

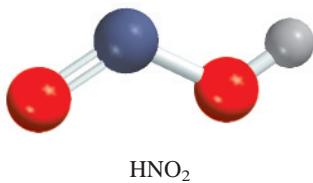
$$[\text{F}^-] = 5.6 \times 10^{-3} \text{ M}$$

The pH of the solution, then, is

$$\text{pH} = -\log(5.6 \times 10^{-3}) = 2.25$$

In summary, the main steps for solving weak acid ionization problems are

- Identify the major species that can affect the pH of the solution. In most cases, we can ignore the ionization of water. We omit the hydroxide ion because its concentration is determined by that of the  $\text{H}^+$  ion.
- Express the equilibrium concentrations of these species in terms of the initial concentration of the acid and a single unknown  $x$ , which represents the change in concentration.
- Write the acid ionization constant ( $K_a$ ) in terms of the equilibrium concentrations. First solve for  $x$  by the approximate method. If the approximation is not valid, use the quadratic equation to solve for  $x$ .
- Having solved for  $x$ , calculate the equilibrium concentrations of all species and/or the pH of the solution.

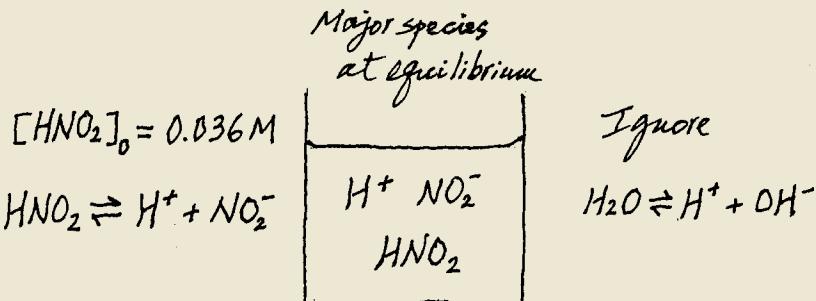


### Example 16.8

Calculate the pH of a 0.036 M nitrous acid (HNO<sub>2</sub>) solution:



**Strategy** Recall that a weak acid only partially ionizes in water. We are given the initial concentration of a weak acid and asked to calculate the pH of the solution at equilibrium. It is helpful to make a sketch to keep track of the pertinent species.



As in Example 16.6, we ignore the ionization of H<sub>2</sub>O so the major source of H<sup>+</sup> ions is the acid. The concentration of OH<sup>-</sup> ions is very small as we would expect from an acidic solution so it is present as a minor species.

**Solution** We follow the procedure already outlined.

*Step 1:* The species that can affect the pH of the solution are HNO<sub>2</sub>, H<sup>+</sup>, and the conjugate base NO<sub>2</sub><sup>-</sup>. We ignore water's contribution to [H<sup>+</sup>].

*Step 2:* Letting  $x$  be the equilibrium concentration of H<sup>+</sup> and NO<sub>2</sub><sup>-</sup> ions in mol/L, we summarize:

|                  | HNO <sub>2</sub> (aq) | H <sup>+</sup> (aq) | + NO <sub>2</sub> <sup>-</sup> (aq) |
|------------------|-----------------------|---------------------|-------------------------------------|
| Initial (M):     | 0.036                 | 0.00                | 0.00                                |
| Change (M):      | - $x$                 | + $x$               | + $x$                               |
| Equilibrium (M): | 0.036 - $x$           | $x$                 | $x$                                 |

*Step 3:* From Table 16.3 we write

$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

$$4.5 \times 10^{-4} = \frac{x^2}{0.036 - x}$$

Applying the approximation  $0.036 - x \approx 0.036$ , we obtain

$$4.5 \times 10^{-4} = \frac{x^2}{0.036 - x} \approx \frac{x^2}{0.036}$$

$$x^2 = 1.62 \times 10^{-5}$$

$$x = 4.0 \times 10^{-3} \text{ M}$$

To test the approximation,

$$\frac{4.0 \times 10^{-3} \text{ M}}{0.036 \text{ M}} \times 100\% = 11\%$$

(Continued)

Because this is greater than 5%, our approximation is not valid and we must solve the quadratic equation, as follows:

$$x^2 + 4.5 \times 10^{-4}x - 1.62 \times 10^{-5} = 0$$

$$x = \frac{-4.5 \times 10^{-4} \pm \sqrt{(4.5 \times 10^{-4})^2 - 4(1)(-1.62 \times 10^{-5})}}{2(1)}$$

$$= 3.8 \times 10^{-3} M \quad \text{or} \quad -4.3 \times 10^{-3} M$$

The second solution is physically impossible, because the concentration of ions produced as a result of ionization cannot be negative. Therefore, the solution is given by the positive root,  $x = 3.8 \times 10^{-3} M$ .

*Step 4:* At equilibrium,

$$[\text{H}^+] = 3.8 \times 10^{-3} M$$

$$\text{pH} = -\log(3.8 \times 10^{-3})$$

$$= 2.42$$

**Check** Note that the calculated pH indicates that the solution is acidic, which is what we would expect for a weak acid solution. Also, compare the calculated pH with that of a 0.036  $M$  strong acid solution such as HCl to convince yourself of the difference between a strong acid and a weak acid.

**Similar problem: 16.45.**

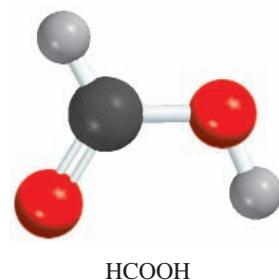
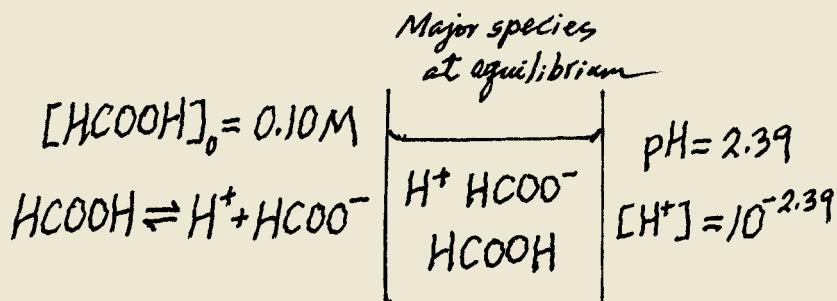
**Practice Exercise** What is the pH of a 0.122  $M$  monoprotic acid whose  $K_a$  is  $5.7 \times 10^{-4}$ ?

One way to determine  $K_a$  of an acid is to measure the pH of the acid solution of known concentration at equilibrium. Example 16.9 shows this approach.

### Example 16.9

The pH of a 0.10  $M$  solution of formic acid ( $\text{HCOOH}$ ) is 2.39. What is the  $K_a$  of the acid?

**Strategy** Formic acid is a weak acid. It only partially ionizes in water. Note that the concentration of formic acid refers to the initial concentration, before ionization has started. The pH of the solution, on the other hand, refers to the equilibrium state. To calculate  $K_a$ , then, we need to know the concentrations of all three species:  $[\text{H}^+]$ ,  $[\text{HCOO}^-]$ , and  $[\text{HCOOH}]$  at equilibrium. As usual, we ignore the ionization of water. The following sketch summarizes the situation.



(Continued)

**Solution** We proceed as follows.

*Step 1:* The major species in solution are HCOOH, H<sup>+</sup>, and the conjugate base HCOO<sup>-</sup>.

*Step 2:* First we need to calculate the hydrogen ion concentration from the pH value

$$\begin{aligned}\text{pH} &= -\log[\text{H}^+] \\ 2.39 &= -\log[\text{H}^+]\end{aligned}$$

Taking the antilog of both sides, we get

$$[\text{H}^+] = 10^{-2.39} = 4.1 \times 10^{-3} M$$

Next we summarize the changes:

|                  | HCOOH(aq)                     | $\rightleftharpoons$ | H <sup>+</sup> (aq)   | + | HCOO <sup>-</sup> (aq) |
|------------------|-------------------------------|----------------------|-----------------------|---|------------------------|
| Initial (M):     | 0.10                          |                      | 0.00                  |   | 0.00                   |
| Change (M):      | $-4.1 \times 10^{-3}$         |                      | $+4.1 \times 10^{-3}$ |   | $+4.1 \times 10^{-3}$  |
| Equilibrium (M): | $(0.10 - 4.1 \times 10^{-3})$ |                      | $4.1 \times 10^{-3}$  |   | $4.1 \times 10^{-3}$   |

Note that because the pH and hence the H<sup>+</sup> ion concentration is known, it follows that we also know the concentrations of HCOOH and HCOO<sup>-</sup> at equilibrium.

*Step 3:* The ionization constant of formic acid is given by

$$\begin{aligned}K_a &= \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} \\ &= \frac{(4.1 \times 10^{-3})(4.1 \times 10^{-3})}{(0.10 - 4.1 \times 10^{-3})} \\ &= 1.8 \times 10^{-4}\end{aligned}$$

**Check** The K<sub>a</sub> value differs slightly from the one listed in Table 16.3 because of the rounding-off procedure we used in the calculation.

**Similar problem:** 16.43.

**Practice Exercise** The pH of a 0.060 M weak monoprotic acid is 3.44. Calculate the K<sub>a</sub> of the acid.

## Percent Ionization

We have seen that the magnitude of K<sub>a</sub> indicates the strength of an acid. Another measure of the strength of an acid is its **percent ionization**, which is defined as

$$\text{percent ionization} = \frac{\text{ionized acid concentration at equilibrium}}{\text{initial concentration of acid}} \times 100\% \quad (16.11)$$

The stronger the acid, the greater the percent ionization. For a monoprotic acid HA, the concentration of the acid that undergoes ionization is equal to the concentration of the H<sup>+</sup> ions or the concentration of the A<sup>-</sup> ions at equilibrium. Therefore, we can write the percent ionization as

$$\text{percent ionization} = \frac{[\text{H}^+]}{[\text{HA}]_0} \times 100\%$$

where [H<sup>+</sup>] is the concentration at equilibrium and [HA]<sub>0</sub> is the initial concentration.

Referring to Example 16.8, we see that the percent ionization of a 0.036 M HNO<sub>2</sub> solution is

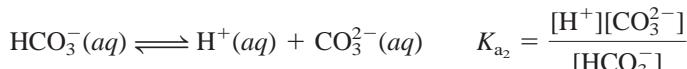
$$\text{percent ionization} = \frac{3.8 \times 10^{-3} M}{0.036 M} \times 100\% = 11\%$$

Thus, only about one out of every 9 HNO<sub>2</sub> molecules has ionized. This is consistent with the fact that HNO<sub>2</sub> is a weak acid.

The extent to which a weak acid ionizes depends on the initial concentration of the acid. The more dilute the solution, the greater the percent ionization (Figure 16.4). In qualitative terms, when an acid is diluted, the concentration of the “particles” in the solution is reduced. According to Le Châtelier’s principle (see Section 15.4), this reduction in particle concentration (the stress) is counteracted by shifting the reaction to the side with more particles; that is, the equilibrium shifts from the nonionized acid side (one particle) to the side containing the H<sup>+</sup> ion and the conjugate base (two particles). Consequently, the percent ionization of the acid increases.

## Diprotic and Polyprotic Acids

Diprotic and polyprotic acids may yield more than one hydrogen ion per molecule. These acids ionize in a stepwise manner, that is, they lose one proton at a time. An ionization constant expression can be written for each ionization stage. Consequently, two or more equilibrium constant expressions must often be used to calculate the concentrations of species in the acid solution. For example, for H<sub>2</sub>CO<sub>3</sub> we write



Note that the conjugate base in the first ionization stage becomes the acid in the second ionization stage.

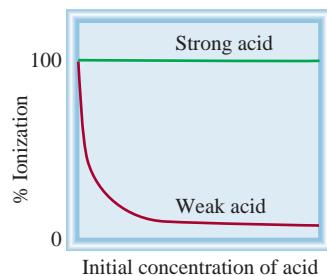
Table 16.4 shows the ionization constants of several diprotic acids and a polyprotic acid. For a given acid, the first ionization constant is much larger than the second ionization constant, and so on. This trend is reasonable because it is easier to remove an H<sup>+</sup> ion from a neutral molecule than to remove another H<sup>+</sup> from a negatively charged ion derived from the molecule.

### Example 16.10

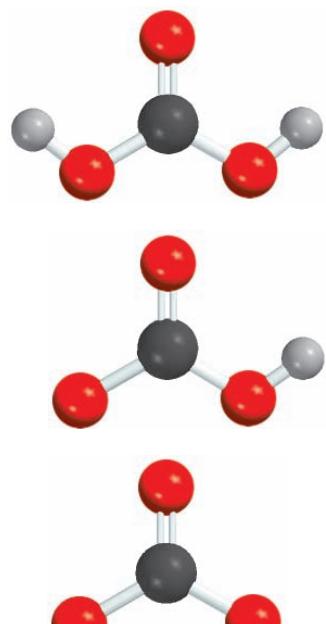
Oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) is a poisonous substance used chiefly as a bleaching and cleansing agent (for example, to remove bathtub rings). Calculate the concentrations of all the species present at equilibrium in a 0.10 M solution.

**Strategy** Determining the equilibrium concentrations of the species of a diprotic acid in aqueous solution is more involved than for a monoprotic acid. We follow the same procedure as that used for a monoprotic acid for each stage, as in Example 16.8. Note that the conjugate base from the first stage of ionization becomes the acid for the second stage ionization.

(Continued)



**Figure 16.4**  
Dependence of percent ionization on initial concentration of acid. Note that at very low concentrations, all acids (weak and strong) are almost completely ionized.



Top to bottom: H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>.

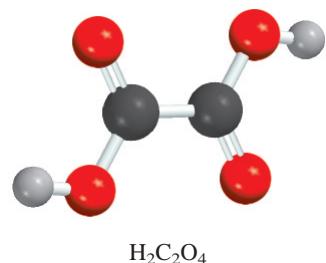


TABLE 16.4

## Ionization Constants of Some Diprotic Acids and a Polyprotic Acid and Their Conjugate Bases at 25°C

| Name of Acid             | Formula                          | Structure   | $K_a$                 | Conjugate Base              | $K_b$                 |
|--------------------------|----------------------------------|---|-----------------------|-----------------------------|-----------------------|
| Sulfuric acid            | $\text{H}_2\text{SO}_4$          | $\begin{array}{c} \text{O} \\    \\ \text{H}-\text{O}-\text{S}-\text{O}-\text{H} \\    \\ \text{O} \end{array}$                 | Very large            | $\text{HSO}_4^-$            | Very small            |
| Hydrogen sulfate ion     | $\text{HSO}_4^-$                 | $\begin{array}{c} \text{O} \\    \\ \text{H}-\text{O}-\text{S}-\text{O}^- \\    \\ \text{O} \end{array}$                        | $1.3 \times 10^{-2}$  | $\text{SO}_4^{2-}$          | $7.7 \times 10^{-13}$ |
| Oxalic acid              | $\text{H}_2\text{C}_2\text{O}_4$ | $\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \text{H}-\text{O}-\text{C}-\text{C}-\text{O}-\text{H} \end{array}$  | $6.5 \times 10^{-2}$  | $\text{HC}_2\text{O}_4^-$   | $1.5 \times 10^{-13}$ |
| Hydrogen oxalate ion     | $\text{HC}_2\text{O}_4^-$        | $\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \text{H}-\text{O}-\text{C}-\text{C}-\text{O}^- \end{array}$         | $6.1 \times 10^{-5}$  | $\text{C}_2\text{O}_4^{2-}$ | $1.6 \times 10^{-10}$ |
| Sulfurous acid*          | $\text{H}_2\text{SO}_3$          | $\begin{array}{c} \text{O} \\    \\ \text{H}-\text{O}-\text{S}-\text{O}-\text{H} \end{array}$                                   | $1.3 \times 10^{-2}$  | $\text{HSO}_3^-$            | $7.7 \times 10^{-13}$ |
| Hydrogen sulfite ion     | $\text{HSO}_3^-$                 | $\begin{array}{c} \text{O} \\    \\ \text{H}-\text{O}-\text{S}-\text{O}^- \end{array}$  | $6.3 \times 10^{-8}$  | $\text{SO}_3^{2-}$          | $1.6 \times 10^{-7}$  |
| Carbonic acid            | $\text{H}_2\text{CO}_3$          | $\begin{array}{c} \text{O} \\    \\ \text{H}-\text{O}-\text{C}-\text{O}-\text{H} \end{array}$                                   | $4.2 \times 10^{-7}$  | $\text{HCO}_3^-$            | $2.4 \times 10^{-8}$  |
| Hydrogen carbonate ion   | $\text{HCO}_3^-$                 | $\begin{array}{c} \text{O} \\    \\ \text{H}-\text{O}-\text{C}-\text{O}^- \end{array}$  | $4.8 \times 10^{-11}$ | $\text{CO}_3^{2-}$          | $2.1 \times 10^{-4}$  |
| Hydrosulfuric acid       | $\text{H}_2\text{S}$             | $\text{H}-\text{S}-\text{H}$  | $9.5 \times 10^{-8}$  | $\text{HS}^-$               | $1.1 \times 10^{-7}$  |
| Hydrogen sulfide ion†    | $\text{HS}^-$                    | $\text{H}-\text{S}^-$   | $1 \times 10^{-19}$   | $\text{S}^{2-}$             | $1 \times 10^5$       |
| Phosphoric acid          | $\text{H}_3\text{PO}_4$          | $\begin{array}{c} \text{O} \\    \\ \text{H}-\text{O}-\text{P}-\text{O}-\text{H} \\   \\ \text{O} \\   \\ \text{H} \end{array}$ | $7.5 \times 10^{-3}$  | $\text{H}_2\text{PO}_4^-$   | $1.3 \times 10^{-12}$ |
| Dihydrogen phosphate ion | $\text{H}_2\text{PO}_4^-$        | $\begin{array}{c} \text{O} \\    \\ \text{H}-\text{O}-\text{P}-\text{O}^- \\   \\ \text{O} \\   \\ \text{H} \end{array}$        | $6.2 \times 10^{-8}$  | $\text{HPO}_4^{2-}$         | $1.6 \times 10^{-7}$  |
| Hydrogen phosphate ion   | $\text{HPO}_4^{2-}$              | $\begin{array}{c} \text{O} \\    \\ \text{H}-\text{O}-\text{P}-\text{O}^- \\   \\ \text{O}^- \end{array}$                       | $4.8 \times 10^{-13}$ | $\text{PO}_4^{3-}$          | $2.1 \times 10^{-2}$  |

\* $\text{H}_2\text{SO}_3$  has never been isolated and exists in only minute concentration in aqueous solution of  $\text{SO}_2$ . The  $K_a$  value here refers to the process  $\text{SO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{HSO}_3^-(aq)$ .

†The ionization constant of  $\text{HS}^-$  is very low and difficult to measure. The value listed here is only an estimate.

**Solution** We proceed according to the following steps:

*Step 1:* The major species in solution at this stage are the nonionized acid,  $\text{H}^+$  ions, and the conjugate base,  $\text{HC}_2\text{O}_4^-$ .

*Step 2:* Letting  $x$  be the equilibrium concentration of  $\text{H}^+$  and  $\text{HC}_2\text{O}_4^-$  ions in mol/L, we summarize:

|                      |                                      |                      |                  |   |                               |
|----------------------|--------------------------------------|----------------------|------------------|---|-------------------------------|
|                      | $\text{H}_2\text{C}_2\text{O}_4(aq)$ | $\rightleftharpoons$ | $\text{H}^+(aq)$ | + | $\text{HC}_2\text{O}_4^-(aq)$ |
| Initial ( $M$ ):     | 0.10                                 |                      | 0.00             |   | 0.00                          |
| Change ( $M$ ):      | $-x$                                 |                      | $+x$             |   | $+x$                          |
| Equilibrium ( $M$ ): | $0.10 - x$                           |                      | $x$              |   | $x$                           |

*Step 3:* Table 16.4 gives us

$$K_a = \frac{[\text{H}^+][\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]}$$

$$6.5 \times 10^{-2} = \frac{x^2}{0.10 - x}$$

Applying the approximation  $0.10 - x \approx 0.10$ , we obtain

$$6.5 \times 10^{-2} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$x^2 = 6.5 \times 10^{-3}$$

$$x = 8.1 \times 10^{-2} M$$

To test the approximation,

$$\frac{8.1 \times 10^{-2} M}{0.10 M} \times 100\% = 81\%$$

Clearly the approximation is not valid. Therefore, we must solve the quadratic equation

$$x^2 + 6.5 \times 10^{-2}x - 6.5 \times 10^{-3} = 0$$

The result is  $x = 0.054 M$ .

*Step 4:* When the equilibrium for the first stage of ionization is reached, the concentrations are

$$[\text{H}^+] = 0.054 M$$

$$[\text{HC}_2\text{O}_4^-] = 0.054 M$$

$$[\text{H}_2\text{C}_2\text{O}_4] = (0.10 - 0.054) M = 0.046 M$$

Next we consider the second stage of ionization.

*Step 1:* At this stage, the major species are  $\text{HC}_2\text{O}_4^-$ , which acts as the acid in the second stage of ionization,  $\text{H}^+$ , and the conjugate base  $\text{C}_2\text{O}_4^{2-}$ .

*Step 2:* Letting  $y$  be the equilibrium concentration of  $\text{H}^+$  and  $\text{C}_2\text{O}_4^{2-}$  ions in mol/L, we summarize:

|                      |                               |                      |                  |   |                                 |
|----------------------|-------------------------------|----------------------|------------------|---|---------------------------------|
|                      | $\text{HC}_2\text{O}_4^-(aq)$ | $\rightleftharpoons$ | $\text{H}^+(aq)$ | + | $\text{C}_2\text{O}_4^{2-}(aq)$ |
| Initial ( $M$ ):     | 0.054                         |                      | 0.054            |   | 0.00                            |
| Change ( $M$ ):      | $-y$                          |                      | $+y$             |   | $+y$                            |
| Equilibrium ( $M$ ): | $0.054 - y$                   |                      | $0.054 + y$      |   | $y$                             |

(Continued)

*Step 3:* Table 16.4 gives us

$$K_a = \frac{[H^+][C_2O_4^{2-}]}{[HC_2O_4^-]}$$

$$6.1 \times 10^{-5} = \frac{(0.054 + y)(y)}{(0.054 - y)}$$

Applying the approximation  $0.054 + y \approx 0.054$  and  $0.054 - y \approx 0.054$ , we obtain

$$\frac{(0.054)(y)}{(0.054)} = y = 6.1 \times 10^{-5} M$$

and we test the approximation,

$$\frac{6.1 \times 10^{-5} M}{0.054 M} \times 100\% = 0.11\%$$

The approximation is valid.

*Step 4:* At equilibrium,

$$[H_2C_2O_4] = 0.046 M$$

$$[HC_2O_4^-] = (0.054 - 6.1 \times 10^{-5}) M = 0.054 M$$

$$[H^+] = (0.054 + 6.1 \times 10^{-5}) M = 0.054 M$$

$$[C_2O_4^{2-}] = 6.1 \times 10^{-5} M$$

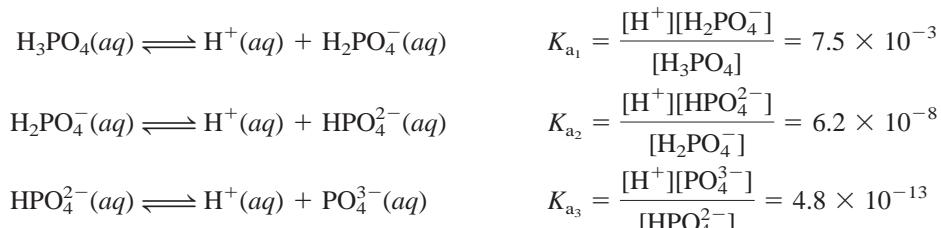
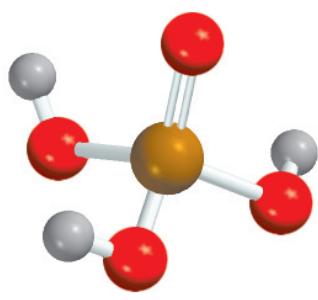
$$[OH^-] = 1.0 \times 10^{-14}/0.054 = 1.9 \times 10^{-13} M$$

**Similar Problem:** 16.52.

**Practice Exercise** Calculate the concentrations of  $H_2C_2O_4$ ,  $HC_2O_4^-$ ,  $C_2O_4^{2-}$ , and  $H^+$  ions in a  $0.20\text{ M}$  oxalic acid solution.

Example 16.10 shows that for diprotic acids, if  $K_{a_1} \gg K_{a_2}$ , then we can assume that the concentration of  $H^+$  ions is the product of only the first stage of ionization. Furthermore, the concentration of the conjugate base for the second-stage ionization is *numerically equal* to  $K_{a_2}$ .

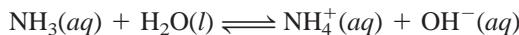
Phosphoric acid ( $H_3PO_4$ ) is a polyprotic acid with three ionizable hydrogen atoms:



We see that phosphoric acid is a weak polyprotic acid and that its ionization constants decrease markedly for the second and third stages. Thus we can predict that, in a solution containing phosphoric acid, the concentration of the nonionized acid is the highest, and the only other species present in significant concentrations are  $H^+$  and  $H_2PO_4^-$  ions.

## 16.6 Weak Bases and Base Ionization Constants

The ionization of weak bases is treated in the same way as the ionization of weak acids. When ammonia dissolves in water, it undergoes the reaction



The equilibrium constant is given by

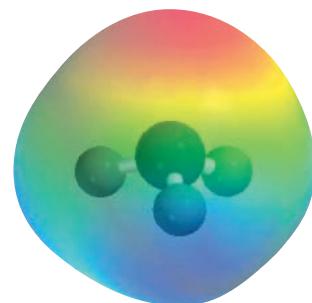
$$K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]}$$

The production of hydroxide ions in this *base ionization reaction* means that  $[\text{OH}^-] > [\text{H}^+]$  and therefore  $\text{pH} > 7$ .

Compared with the total concentration of water, very few water molecules are consumed by this reaction, so we can treat  $[\text{H}_2\text{O}]$  as a constant. Thus we can write the **base ionization constant ( $K_b$ )**, which is the *equilibrium constant for the ionization reaction*, as

$$K_b = K[\text{H}_2\text{O}] = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

Table 16.5 lists a number of common weak bases and their ionization constants. Note that the basicity of all these compounds is attributable to the lone pair of electrons on the nitrogen atom. The ability of the lone pair to accept a  $\text{H}^+$  ion makes these substances Brønsted bases.



Electrostatic potential map of  $\text{NH}_3$ . The lone pair (red color) on the N atom accounts for ammonia's basicity.

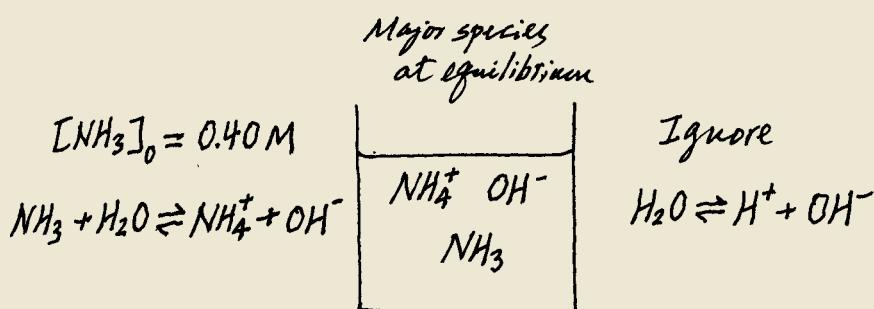


**Animation:**  
Base Ionization  
ARIS, Animations

### Example 16.11

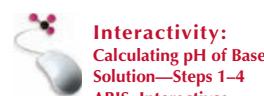
What is the pH of a 0.40 M ammonia solution?

**Strategy** The procedure here is similar to the one used for a weak acid (see Example 16.8). From the ionization of ammonia, we see that the major species in solution at equilibrium are  $\text{NH}_3$ ,  $\text{NH}_4^+$ , and  $\text{OH}^-$ . The hydrogen ion concentration is very small as we would expect from a basic solution, so it is present as a minor species. As before, we ignore the ionization of water. We make a sketch to keep track of the pertinent species as follows:



**Solution** We proceed according to the following steps:

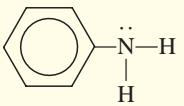
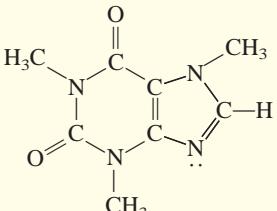
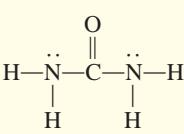
**Step 1:** The major species in an ammonia solution are  $\text{NH}_3$ ,  $\text{NH}_4^+$ , and  $\text{OH}^-$ . We ignore the very small contribution to  $\text{OH}^-$  concentration by water.



**Interactivity:**  
Calculating pH of Base  
Solution—Steps 1–4  
ARIS, Interactives

(Continued)

**TABLE 16.5** Ionization Constants of Some Weak Bases and Their Conjugate Acids at 25°C

| Name of Base | Formula                                       | Structure  | $K_b^*$               | Conjugate Acid   | $K_a$                 |
|--------------|---|--|-----------------------|--|-----------------------|
| Ethylamine   | $\text{C}_2\text{H}_5\text{NH}_2$             | $\text{CH}_3-\text{CH}_2-\overset{\cdot\cdot}{\underset{\text{H}}{\text{N}}}-\text{H}$ | $5.6 \times 10^{-4}$  | $\text{C}_2\text{H}_5\overset{+}{\text{NH}_3}$             | $1.8 \times 10^{-11}$ |
| Methylamine  | $\text{CH}_3\text{NH}_2$                      | $\text{CH}_3-\overset{\cdot\cdot}{\underset{\text{H}}{\text{N}}}-\text{H}$             | $4.4 \times 10^{-4}$  | $\text{CH}_3\overset{+}{\text{NH}_3}$                      | $2.3 \times 10^{-11}$ |
| Ammonia      | $\text{NH}_3$                                 | $\text{H}-\overset{\cdot\cdot}{\underset{\text{H}}{\text{N}}}-\text{H}$                | $1.8 \times 10^{-5}$  | $\text{NH}_4^+$  | $5.6 \times 10^{-10}$ |
| Pyridine     | $\text{C}_5\text{H}_5\text{N}$                |       | $1.7 \times 10^{-9}$  | $\text{C}_5\text{H}_5\overset{+}{\text{NH}}$               | $5.9 \times 10^{-6}$  |
| Aniline      | $\text{C}_6\text{H}_5\text{NH}_2$             |       | $3.8 \times 10^{-10}$ | $\text{C}_6\text{H}_5\overset{+}{\text{NH}_3}$             | $2.6 \times 10^{-5}$  |
| Caffeine     | $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ |      | $5.3 \times 10^{-14}$ | $\text{C}_8\text{H}_{11}\overset{+}{\text{N}_4}\text{O}_2$ | 0.19                  |
| Urea         | $(\text{NH}_2)_2\text{CO}$                    |     | $1.5 \times 10^{-14}$ | $\text{H}_2\text{NCONH}_3^+$                               | 0.67                  |

\*The nitrogen atom with the lone pair accounts for each compound's basicity. In the case of urea,  $K_b$  can be associated with either nitrogen atom.

*Step 2:* Letting  $x$  be the equilibrium concentration of  $\text{NH}_4^+$  and  $\text{OH}^-$  ions in mol/L, we summarize:

|                      |                   |  |                     |                     |
|----------------------|-------------------|--|---------------------|---------------------|
|                      | $\text{NH}_3(aq)$ | $+ \text{H}_2\text{O}(l) \rightleftharpoons$ | $\text{NH}_4^+(aq)$ | $+ \text{OH}^-(aq)$ |
| Initial ( $M$ ):     |                   |  | 0.40                | 0.00                |
| Change ( $M$ ):      |                   |  | $-x$                | $+x$                |
| Equilibrium ( $M$ ): |                   |  | $0.40 - x$          | $x$                 |

*Step 3:* Table 16.5 gives us  $K_b$ :

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.40 - x}$$

(Continued)

Applying the approximation  $0.40 - x \approx 0.40$ , we obtain

$$\begin{aligned} 1.8 \times 10^{-5} &= \frac{x^2}{0.40 - x} \approx \frac{x^2}{0.40} \\ x^2 &= 7.2 \times 10^{-6} \\ x &= 2.7 \times 10^{-3} M \end{aligned}$$

To test the approximation, we write

$$\frac{2.7 \times 10^{-3} M}{0.40 M} \times 100\% = 0.68\%$$

**The 5 percent rule (p. 542) also applies to bases.**

Therefore, the approximation is valid.

*Step 4:* At equilibrium,  $[\text{OH}^-] = 2.7 \times 10^{-3} M$ . Thus,

$$\begin{aligned} \text{pOH} &= -\log(2.7 \times 10^{-3}) \\ &= 2.57 \end{aligned}$$

From Equation (16.9)

$$\begin{aligned} \text{pH} &= 14.00 - 2.57 \\ &= 11.43 \end{aligned}$$

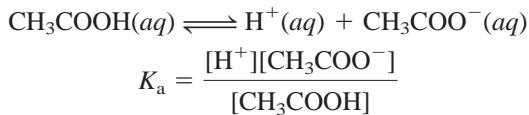
**Check** Note that the pH calculated is basic, which is what we would expect from a weak base solution. Compare the calculated pH with that of a  $0.40 M$  strong base solution, such as KOH, to convince yourself of the difference between a strong base and a weak base.

**Similar Problem: 16.55.**

**Practice Exercise** Calculate the pH of a  $0.26 M$  methylamine solution (see Table 16.5).

## 16.7 The Relationship Between Conjugate Acid-Base Ionization Constants

An important relationship between the acid ionization constant and the ionization constant of its conjugate base can be derived as follows, using acetic acid as an example:



The conjugate base,  $\text{CH}_3\text{COO}^-$ , reacts with water according to the equation



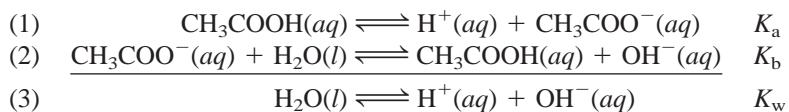
and we can write the base ionization constant as

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

The product of these two ionization constants is given by

$$\begin{aligned} K_a K_b &= \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \times \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \\ &= [\text{H}^+][\text{OH}^-] \\ &= K_w \end{aligned}$$

This result may seem strange at first, but it can be understood by realizing that the sum of reactions (1) and (2) here is simply the autoionization of water.



This example illustrates one of the rules for chemical equilibria: When two reactions are added to give a third reaction, the equilibrium constant for the third reaction is the product of the equilibrium constants for the two added reactions. Thus, for any conjugate acid-base pair it is always true that

$$K_a K_b = K_w \quad (16.12)$$

To find  $K_a$ , you must use the  $K_b$  of the conjugate base formed in the ionization of the acid and vice versa.

Expressing Equation (16.12) as

$$K_a = \frac{K_w}{K_b} \quad K_b = \frac{K_w}{K_a}$$

enables us to draw an important conclusion: The stronger the acid (the larger  $K_a$ ), the weaker its conjugate base (the smaller  $K_b$ ), and vice versa (see Tables 16.3, 16.4, and 16.5).

We can use Equation (16.12) to calculate the  $K_b$  of the conjugate base ( $\text{CH}_3\text{COO}^-$ ) of  $\text{CH}_3\text{COOH}$  as follows. We find the  $K_a$  value of  $\text{CH}_3\text{COOH}$  in Table 16.3 and write

$$\begin{aligned} K_b &= \frac{K_w}{K_a} \\ &= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \\ &= 5.6 \times 10^{-10} \end{aligned}$$

## 16.8 Molecular Structure and the Strength of Acids



**Interactivity:**  
Molecular Structure and Acid Strength  
ARIS, Interactives

The strength of an acid depends on a number of factors, such as the properties of the solvent, the temperature, and, of course, the molecular structure of the acid. When we compare the strengths of two acids, we can eliminate some variables by considering their properties in the same solvent and at the same temperature and concentration. Then we can focus on the structure of the acids.

Let us consider a certain acid  $\text{HX}$ . The strength of the acid is measured by its tendency to ionize:



Two factors influence the extent to which the acid undergoes ionization. One is the strength of the H—X bond—the stronger the bond, the more difficult it is for the  $\text{HX}$  molecule to break up and hence the *weaker* the acid. The other factor is the polarity of the H—X bond. The difference in the electronegativities between H and X results in a polar bond like



**TABLE 16.6****Bond Enthalpies for Hydrogen Halides and Acid Strength for Hydrohalic Acids**

| Bond | Bond Enthalpy (kJ/mol) | Acid Strength |
|------|------------------------|---------------|
| H—F  | 568.2                  | weak          |
| H—Cl | 431.9                  | strong        |
| H—Br | 366.1                  | strong        |
| H—I  | 298.3                  | strong        |

If the bond is highly polarized, that is, if there is a large accumulation of positive and negative charges on the H and X atoms, HX will tend to break up into  $\text{H}^+$  and  $\text{X}^-$  ions. So a high degree of polarity characterizes a *stronger* acid. Next we will consider some examples in which either bond strength or bond polarity plays a prominent role in determining acid strength.

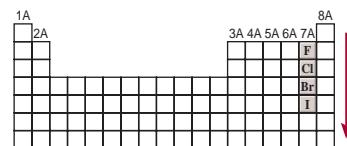
## Hydrohalic Acids

The halogens form a series of binary acids called the hydrohalic acids (HF, HCl, HBr, and HI). Of this series, which factor (bond strength or bond polarity) is the predominant factor in determining the strength of the binary acids? Consider first the strength of the H—X bond in each of these acids. Table 16.6 shows that HF has the highest bond enthalpy of the four hydrogen halides, and HI has the lowest bond enthalpy. It takes 568.2 kJ/mol to break the H—F bond and only 298.3 kJ/mol to break the H—I bond. Based on bond enthalpy, HI should be the strongest acid because it is easiest to break the bond and form the  $\text{H}^+$  and  $\text{I}^-$  ions. Second, consider the polarity of the H—X bond. In this series of acids, the polarity of the bond decreases from HF to HI because F is the most electronegative of the halogens (see Figure 9.4). Based on bond polarity, then, HF should be the strongest acid because of the largest accumulation of positive and negative charges on the H and F atoms. Thus, we have two competing factors to consider in determining the strength of binary acids. The fact that HI is a strong acid and that HF is a weak acid indicates that bond enthalpy is the predominant factor in determining the acid strength of binary acids. In this series of binary acids, the weaker the bond, the stronger the acid so that the strength of the acids increases as follows:



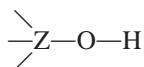
## Oxoacids

Now let us consider the oxoacids. Oxoacids, as we learned in Chapter 2, contain hydrogen, oxygen, and one other element Z, which occupies a central position. Figure 16.5 shows the Lewis structures of several common oxoacids. As you can see, these acids are characterized by the presence of one or more O—H bonds. The central atom Z might also have other groups attached to it:



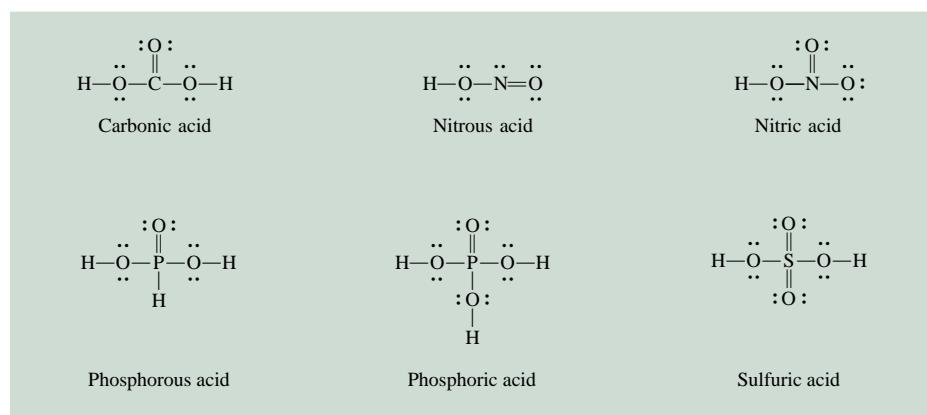
Strength of hydrohalic acids increases from HF to HI.

To review the nomenclature of inorganic acids, see Section 2.8.



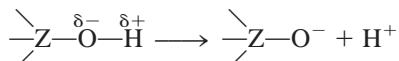
**Figure 16.5**

Lewis structures of some common oxoacids. For simplicity, the formal charges have been omitted.



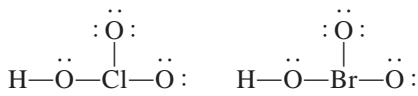
As the oxidation number of an atom becomes larger, its ability to draw electrons in a bond toward itself increases.

If Z is an electronegative element, or is in a high oxidation state, it will attract electrons, thus making the Z—O bond more covalent and the O—H bond more polar. Consequently, the tendency for the hydrogen to be donated as a H<sup>+</sup> ion increases:



To compare their strengths, it is convenient to divide the oxoacids into two groups.

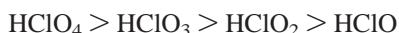
- 1. Oxoacids Having Different Central Atoms That Are from the Same Group of the Periodic Table and That Have the Same Oxidation Number.** Within this group, acid strength increases with increasing electronegativity of the central atom, as  $\text{HClO}_3$  and  $\text{HBrO}_3$  illustrate:

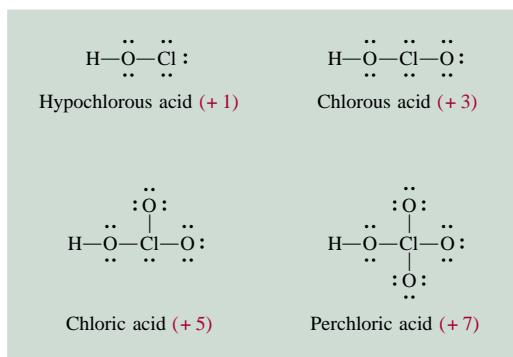


Cl and Br have the same oxidation number, +5. However, because Cl is more electronegative than Br, it attracts the electron pair it shares with oxygen (in the Cl—O—H group) to a greater extent than Br does. Consequently, the O—H bond is more polar in chloric acid than in bromic acid and ionizes more readily. Thus, the relative acid strengths are



2. *Oxoacids Having the Same Central Atom but Different Numbers of Attached Groups.* Within this group, acid strength increases as the oxidation number of the central atom increases. Consider the oxoacids of chlorine shown in Figure 16.6. In this series, the ability of chlorine to draw electrons away from the OH group (thus making the O—H bond more polar) increases with the number of electronegative O atoms attached to Cl. Thus,  $\text{HClO}_4$  is the strongest acid because it has the largest number of O atoms attached to Cl, and the acid strength decreases as follows:



**Figure 16.6**

*Lewis structures of the oxoacids of chlorine. The oxidation number of the Cl atom is shown in parentheses. For simplicity, the formal charges have been omitted. Note that although hypochlorous acid is written as  $\text{HClO}$ , the H atom is bonded to the O atom.*

### Example 16.12

Predict the relative strengths of the oxoacids in each of the following groups: (a)  $\text{HClO}$ ,  $\text{HBrO}$ , and  $\text{HIO}$ ; (b)  $\text{HNO}_3$  and  $\text{HNO}_2$ .

**Strategy** Examine the molecular structure. In (a) the two acids have similar structure but differ only in the central atom (Cl, Br, and I). Which central atom is the most electronegative? In (b) the acids have the same central atom (N) but differ in the number of O atoms. What is the oxidation number of N in each of these two acids?

**Solution** (a) These acids all have the same structure, and the halogens all have the same oxidation number (+1). Because the electronegativity decreases from Cl to I, the polarity of the X—O bond (where X denotes a halogen atom) increases from  $\text{HClO}$  to  $\text{HIO}$ , and the polarity of the O—H bond decreases from  $\text{HClO}$  to  $\text{HIO}$ . Thus, the acid strength decreases as follows:



(b) The structures of  $\text{HNO}_3$  and  $\text{HNO}_2$  are shown in Figure 16.5. Because the oxidation number of N is +5 in  $\text{HNO}_3$  and +3 in  $\text{HNO}_2$ ,  $\text{HNO}_3$  is a stronger acid than  $\text{HNO}_2$ .

**Similar problem: 16.62.**

**Practice Exercise** Which of the following acids is weaker:  $\text{HClO}_3$  or  $\text{HClO}_2$ ?

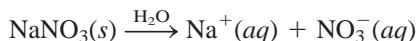
## 16.9 Acid-Base Properties of Salts

As defined in Section 4.3, a salt is an ionic compound formed by the reaction between an acid and a base. Salts are strong electrolytes that completely dissociate in water and in some cases react with water. The term *salt hydrolysis* describes the reaction of an anion or a cation of a salt, or both, with water. Salt hydrolysis usually affects the pH of a solution.

*The word “hydrolysis” is derived from the Greek words *hydro*, meaning “water,” and *lysis*, meaning “to split apart.”*

### Salts That Produce Neutral Solutions

It is generally true that salts containing an alkali metal ion or alkaline earth metal ion (except  $\text{Be}^{2+}$ ) and the conjugate base of a strong acid (for example,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{NO}_3^-$ ) do not undergo hydrolysis to an appreciable extent, and their solutions are assumed to be neutral. For instance, when  $\text{NaNO}_3$ , a salt formed by the reaction of  $\text{NaOH}$  with  $\text{HNO}_3$ , dissolves in water, it dissociates completely as



**In reality, all positive ions give acid solutions in water.**

The mechanism by which metal ions produce acid solutions is discussed on p. 560.

The hydrated  $\text{Na}^+$  ion neither donates nor accepts  $\text{H}^+$  ions. The  $\text{NO}_3^-$  ion is the conjugate base of the strong acid  $\text{HNO}_3$ , and it has no affinity for  $\text{H}^+$  ions. Consequently, a solution containing  $\text{Na}^+$  and  $\text{NO}_3^-$  ions is neutral, with a pH of 7.



## Salts That Produce Basic Solutions

The dissociation of sodium acetate ( $\text{CH}_3\text{COONa}$ ) in water is given by



The hydrated  $\text{Na}^+$  ion has no acidic or basic properties. The acetate ion  $\text{CH}_3\text{COO}^-$ , however, is the conjugate base of the weak acid  $\text{CH}_3\text{COOH}$  and therefore has an affinity for  $\text{H}^+$  ions. The hydrolysis reaction is given by



Because this reaction produces  $\text{OH}^-$  ions, the sodium acetate solution will be basic. The equilibrium constant for this hydrolysis reaction is the base ionization constant expression for  $\text{CH}_3\text{COO}^-$ , so we write

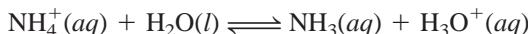
$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = 5.6 \times 10^{-10}$$

## Salts That Produce Acidic Solutions

When a salt derived from a strong acid and a weak base dissolves in water, the solution becomes acidic. For example, consider the process



The  $\text{Cl}^-$  ion has no affinity for  $\text{H}^+$  ions. The ammonium ion  $\text{NH}_4^+$  is the weak conjugate acid of the weak base  $\text{NH}_3$  and ionizes as



or simply



Because this reaction produces  $\text{H}^+$  ions, the pH of the solution decreases. As you can see, the hydrolysis of the  $\text{NH}_4^+$  ion is the same as the ionization of the  $\text{NH}_4^+$  acid. The equilibrium constant (or ionization constant) for this process is given by

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-10}} = 5.6 \times 10^{-10}$$

By coincidence,  $K_a$  of  $\text{NH}_4^+$  has the same numerical value as  $K_b$  of  $\text{CH}_3\text{COO}^-$ .

In solving salt hydrolysis problems, we follow the same procedure we used for weak acids and weak bases.

### Example 16.13

Calculate the pH of a  $0.15\text{ M}$  solution of sodium acetate ( $\text{CH}_3\text{COONa}$ ). What is the percent hydrolysis?

**Strategy** What is a salt? In solution,  $\text{CH}_3\text{COONa}$  dissociates completely into  $\text{Na}^+$  and  $\text{CH}_3\text{COO}^-$  ions. The  $\text{Na}^+$  ion, as we saw earlier, does not react with water and has no effect on the pH of the solution. The  $\text{CH}_3\text{COO}^-$  ion is the conjugate base of the weak acid  $\text{CH}_3\text{COOH}$ . Therefore, we expect that it will react to a certain extent with water to produce  $\text{CH}_3\text{COOH}$  and  $\text{OH}^-$ , and the solution will be basic.

#### Solution

*Step 1:* Because we started with a  $0.15\text{ M}$  sodium acetate solution, the concentrations of the ions are also equal to  $0.15\text{ M}$  after dissociation:

|                  |   |       |       |
|------------------|---|-------|-------|
|                  | $\text{CH}_3\text{COONa}(aq) \longrightarrow \text{Na}^+(aq) + \text{CH}_3\text{COO}^-(aq)$ |       |       |
| Initial ( $M$ ): | 0.15  | 0     | 0     |
| Change ( $M$ ):  | -0.15   | +0.15 | +0.15 |
| Final ( $M$ ):   | 0   | 0.15  | 0.15  |

Of these ions, only the acetate ion will react with water



At equilibrium, the major species in solution are  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COO}^-$ , and  $\text{OH}^-$ . The concentration of the  $\text{H}^+$  ion is very small as we would expect for a basic solution, so it is treated as a minor species. We ignore the ionization of water.

*Step 2:* Let  $x$  be the equilibrium concentration of  $\text{CH}_3\text{COOH}$  and  $\text{OH}^-$  ions in mol/L, we summarize:

|                      |   |       |       |
|----------------------|---|-------|-------|
|                      | $\text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COOH}(aq) + \text{OH}^-(aq)$ |       |       |
| Initial ( $M$ ):     | 0.15  | 0.00  | 0.00  |
| Change ( $M$ ):      | - $x$   | + $x$ | + $x$ |
| Equilibrium ( $M$ ): | $0.15 - x$  | $x$   | $x$   |

*Step 3:* From the preceding discussion and Table 16.3 we write the equilibrium constant of hydrolysis, or the base ionization constant, as

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$5.6 \times 10^{-10} = \frac{x^2}{0.15 - x}$$

Because  $K_b$  is very small and the initial concentration of the base is large, we can apply the approximation  $0.15 - x \approx 0.15$ :

$$5.6 \times 10^{-10} = \frac{x^2}{0.15 - x} \approx \frac{x^2}{0.15}$$

$$x = 9.2 \times 10^{-6}\text{ M}$$

(Continued)

*Step 4:* At equilibrium:

$$\begin{aligned} [\text{OH}^-] &= 9.2 \times 10^{-6} M \\ \text{pOH} &= -\log (9.2 \times 10^{-6}) \\ &= 5.04 \\ \text{pH} &= 14.00 - 5.04 \\ &= 8.96 \end{aligned}$$

Thus the solution is basic, as we would expect. The percent hydrolysis is given by

$$\begin{aligned} \% \text{ hydrolysis} &= \frac{[\text{CH}_3\text{COO}^-]_{\text{hydrolyzed}}}{[\text{CH}_3\text{COO}^-]_{\text{initial}}} \\ &= \frac{9.2 \times 10^{-6} M}{0.15 M} \times 100\% \\ &= 0.0061\% \end{aligned}$$

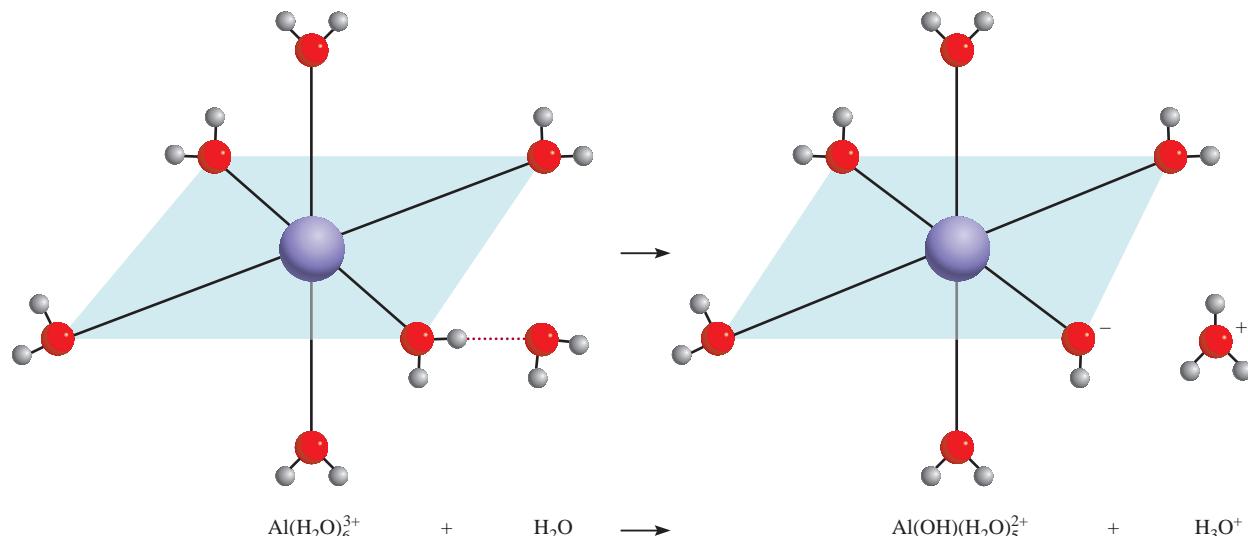
**Check** The result shows that only a very small amount of the anion undergoes hydrolysis. Note that the calculation of percent hydrolysis takes the same form as the test for the approximation, which is valid in this case.

**Similar problem:** 16.73.

**Practice Exercise** Calculate the pH of a 0.24 M sodium formate solution ( $\text{HCOONa}$ ).

## Metal Ion Hydrolysis

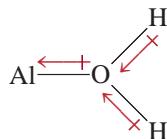
Salts that contain small, highly charged metal cations (for example,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$ , and  $\text{Be}^{2+}$ ) and the conjugate bases of strong acids also produce an acidic solution. For example, when aluminum chloride ( $\text{AlCl}_3$ ) dissolves in water, the  $\text{Al}^{3+}$  ions take the hydrated form  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  (Figure 16.7). Let us consider one



**Figure 16.7**

The six  $\text{H}_2\text{O}$  molecules surround the  $\text{Al}^{3+}$  ion octahedrally. The attraction of the small  $\text{Al}^{3+}$  ion for the lone pairs on the oxygen atoms is so great that the O—H bonds in a  $\text{H}_2\text{O}$  molecule attached to the metal cation are weakened, allowing the loss of a proton ( $\text{H}^+$ ) to an incoming  $\text{H}_2\text{O}$  molecule. This hydrolysis of the metal cation makes the solution acidic.

bond between the metal ion and the oxygen atom of one of the six water molecules in  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ :



The positively charged  $\text{Al}^{3+}$  ion draws electron density toward itself, making the O—H bond more polar. Consequently, the H atoms have a greater tendency to ionize than those in water molecules not involved in hydration. The resulting ionization process can be written as



or simply



The hydrated  $\text{Al}^{3+}$  qualifies as a proton donor and thus a Brønsted acid in this reaction.

The equilibrium constant for the metal cation hydrolysis is given by

$$K_a = \frac{[\text{Al(OH)(H}_2\text{O})_5^{2+}][\text{H}^+]}{[\text{Al}(\text{H}_2\text{O})_6^{3+}]} = 1.3 \times 10^{-5}$$

Note that  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  is roughly as strong an acid as  $\text{CH}_3\text{COOH}$ .

Note that the  $\text{Al(OH)(H}_2\text{O})_5^{2+}$  species can undergo further ionization as



and so on. However, generally it is sufficient to consider only the first step of hydrolysis.

The extent of hydrolysis is greatest for the smallest and most highly charged ions because a “compact” highly charged ion is more effective in polarizing the O—H bond and facilitating ionization. This is the reason that relatively large ions of low charge such as  $\text{Na}^+$  and  $\text{K}^+$  do not undergo hydrolysis to any appreciable extent.

## Salts in Which Both the Cation and the Anion Hydrolyze

So far we have considered salts in which only one ion undergoes hydrolysis. For salts derived from a weak acid and a weak base, both the cation and the anion hydrolyze. However, whether a solution containing such a salt is acidic, basic, or neutral depends on the relative strengths of the weak acid and the weak base. Because the mathematics associated with this type of system is rather involved, we will focus on making qualitative predictions about these solutions based on the following guidelines:

- **$K_b > K_a$ .** If  $K_b$  for the anion is greater than  $K_a$  for the cation, then the solution must be basic because the anion will hydrolyze to a greater extent than the cation. At equilibrium, there will be more  $\text{OH}^-$  ions than  $\text{H}^+$  ions.
- **$K_b < K_a$ .** Conversely, if  $K_b$  for the anion is smaller than  $K_a$  for the cation, the solution will be acidic because cation hydrolysis will be more extensive than anion hydrolysis.
- **$K_b \approx K_a$ .** If  $K_a$  is approximately equal to  $K_b$ , the solution will be nearly neutral.

Table 16.7 summarizes the behavior in aqueous solution of the salts discussed in this section.

**TABLE 16.7 Acid-Base Properties of Salts**

| Type of Salt   | Examples  | Ions That Undergo Hydrolysis | pH of Solution   |
|--|---|------------------------------|--|
| Cation from strong base; anion from strong acid      | NaCl, KI, KNO <sub>3</sub> , RbBr, BaCl <sub>2</sub>                                      | None                         | ≈ 7  |
| Cation from strong base; anion from weak acid        | CH <sub>3</sub> COONa, KNO <sub>2</sub>   | Anion                        | > 7  |
| Cation from weak base; anion from strong acid        | NH <sub>4</sub> Cl, NH <sub>4</sub> NO <sub>3</sub>                                       | Cation                       | < 7  |
| Cation from weak base; anion from weak acid          | NH <sub>4</sub> NO <sub>2</sub> , CH <sub>3</sub> COONH <sub>4</sub> , NH <sub>4</sub> CN | Anion and cation             | < 7 if $K_b < K_a$<br>≈ 7 if $K_b \approx K_a$<br>> 7 if $K_b > K_a$ |
| Small, highly charged cation; anion from strong acid | AlCl <sub>3</sub> , Fe(NO <sub>3</sub> ) <sub>3</sub>                                     | Hydrated cation              | < 7  |

### Example 16.14

Predict whether the following solutions will be acidic, basic, or nearly neutral:  
 (a) NH<sub>4</sub>I, (b) NaNO<sub>2</sub>, (c) FeCl<sub>3</sub>, (d) NH<sub>4</sub>F.

**Strategy** In deciding whether a salt will undergo hydrolysis, ask yourself the following questions: Is the cation a highly charged metal ion or an ammonium ion? Is the anion the conjugate base of a weak acid? If yes to either question, then hydrolysis will occur. In cases where both the cation and the anion react with water, the pH of the solution will depend on the relative magnitudes of  $K_a$  for the cation and  $K_b$  for the anion (see Table 16.7).

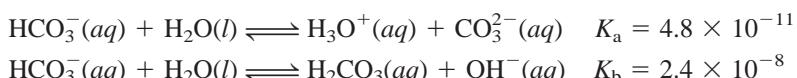
**Solution** We first break up the salt into its cation and anion components and then examine the possible reaction of each ion with water.

- (a) The cation is NH<sub>4</sub><sup>+</sup>, which will hydrolyze to produce NH<sub>3</sub> and H<sup>+</sup>. The I<sup>-</sup> anion is the conjugate base of the strong acid HI. Therefore, I<sup>-</sup> will not hydrolyze and the solution is acidic.
- (b) The Na<sup>+</sup> cation does not hydrolyze. The NO<sub>2</sub><sup>-</sup> is the conjugate base of the weak acid HNO<sub>2</sub> and will hydrolyze to give HNO<sub>2</sub> and OH<sup>-</sup>. The solution will be basic.
- (c) Fe<sup>3+</sup> is a small metal ion with a high charge and hydrolyzes to produce H<sup>+</sup> ions. The Cl<sup>-</sup> does not hydrolyze. Consequently, the solution will be acidic.
- (d) Both the NH<sub>4</sub><sup>+</sup> and F<sup>-</sup> ions will hydrolyze. From Tables 16.5 and 16.3 we see that the  $K_a$  of NH<sub>4</sub><sup>+</sup> ( $5.6 \times 10^{-10}$ ) is greater than the  $K_b$  for F<sup>-</sup> ( $1.4 \times 10^{-11}$ ). Therefore, the solution will be acidic.

**Similar problem:** 16.69.

**Practice Exercise** Predict whether the following solutions will be acidic, basic, or nearly neutral: (a) LiClO<sub>4</sub>, (b) Na<sub>3</sub>PO<sub>4</sub>, (c) Bi(NO<sub>3</sub>)<sub>2</sub>, (d) NH<sub>4</sub>CN.

Finally we note that some anions can act either as an acid or as a base. For example, the bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) can ionize or undergo hydrolysis as follows (see Table 16.4):



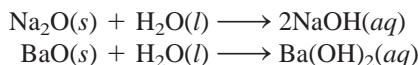
Because  $K_b > K_a$ , we predict that the hydrolysis reaction will outweigh the ionization process. Thus, a solution of sodium bicarbonate (NaHCO<sub>3</sub>) will be basic.

## 16.10 Acidic, Basic, and Amphoteric Oxides

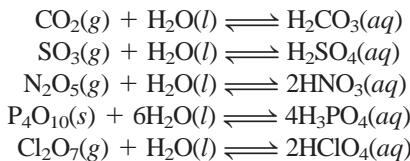
As we saw in Chapter 8, oxides can be classified as acidic, basic, or amphoteric. Our discussion of acid-base reactions would be incomplete without examining the properties of these compounds.

Figure 16.8 shows the formulas of a number of oxides of the representative elements in their highest oxidation states. Note that all alkali metal oxides and all alkaline earth metal oxides except BeO are basic. Beryllium oxide and several metallic oxides in Groups 3A and 4A are amphoteric. Nonmetallic oxides in which the oxidation number of the representative element is high are acidic (for example,  $\text{N}_2\text{O}_5$ ,  $\text{SO}_3$ , and  $\text{Cl}_2\text{O}_7$ ). Those in which the oxidation number of the representative element is low (for example, CO and NO) show no measurable acidic properties. No nonmetallic oxides are known to have basic properties.

The basic metallic oxides react with water to form metal hydroxides:



The reactions between acidic oxides and water are



The reaction between  $\text{CO}_2$  and  $\text{H}_2\text{O}$  explains why when pure water is exposed to air (which contains  $\text{CO}_2$ ) it gradually reaches a pH of about 5.5 (Figure 16.9). The reaction between  $\text{SO}_3$  and  $\text{H}_2\text{O}$  is largely responsible for acid rain.



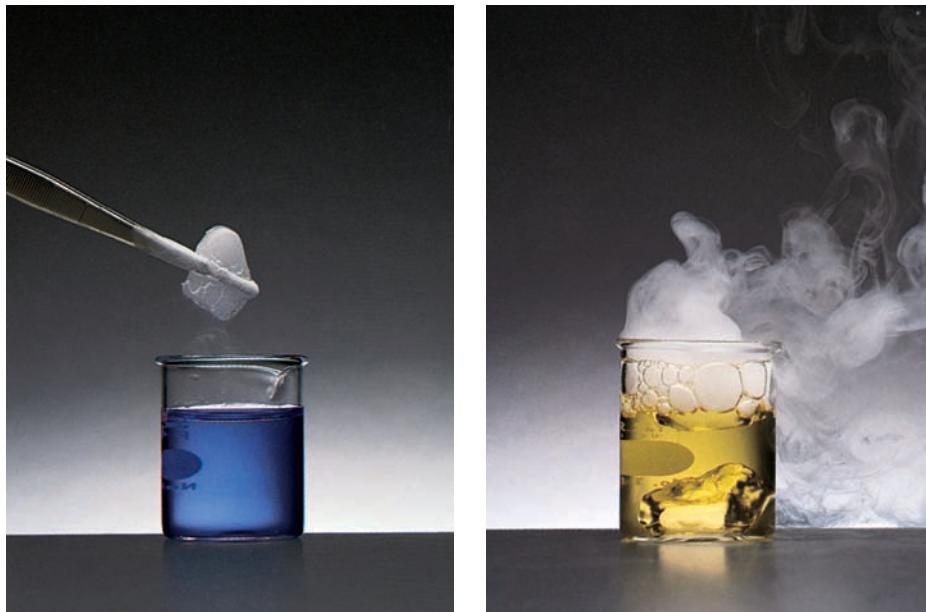
A forest damaged by acid rain.

| 1<br>1A               | 2<br>2A      | Basic oxide |         | Amphoteric oxide |         |         |   |   |    |          |          |                         |                | 13<br>3A                  | 14<br>4A       | 15<br>5A                | 16<br>6A | 17<br>7A      | 18<br>8A |
|-----------------------|--------------|-------------|---------|------------------|---------|---------|---|---|----|----------|----------|-------------------------|----------------|---------------------------|----------------|-------------------------|----------|---------------|----------|
| $\text{Li}_2\text{O}$ | $\text{BeO}$ |             |         |                  |         |         |   |   |    |          |          |                         |                | $\text{B}_2\text{O}_3$    | $\text{CO}_2$  | $\text{N}_2\text{O}_5$  |          | $\text{OF}_2$ |          |
| $\text{Na}_2\text{O}$ | $\text{MgO}$ | 3<br>3B     | 4<br>4B | 5<br>5B          | 6<br>6B | 7<br>7B | 8 | 9 | 10 | 11<br>1B | 12<br>2B | $\text{Al}_2\text{O}_3$ | $\text{SiO}_2$ | $\text{P}_4\text{O}_{10}$ | $\text{SO}_3$  | $\text{Cl}_2\text{O}_7$ |          |               |          |
| $\text{K}_2\text{O}$  | $\text{CaO}$ |             |         |                  |         |         |   |   |    |          |          | $\text{Ga}_2\text{O}_3$ | $\text{GeO}_2$ | $\text{As}_2\text{O}_5$   | $\text{SeO}_3$ | $\text{Br}_2\text{O}_7$ |          |               |          |
| $\text{Rb}_2\text{O}$ | $\text{SrO}$ |             |         |                  |         |         |   |   |    |          |          | $\text{In}_2\text{O}_3$ | $\text{SnO}_2$ | $\text{Sb}_2\text{O}_5$   | $\text{TeO}_3$ | $\text{I}_2\text{O}_7$  |          |               |          |
| $\text{Cs}_2\text{O}$ | $\text{BaO}$ |             |         |                  |         |         |   |   |    |          |          | $\text{Tl}_2\text{O}_3$ | $\text{PbO}_2$ | $\text{Bi}_2\text{O}_5$   | $\text{PoO}_3$ | $\text{At}_2\text{O}_7$ |          |               |          |
|                       |              |             |         |                  |         |         |   |   |    |          |          |                         |                |                           |                |                         |          |               |          |

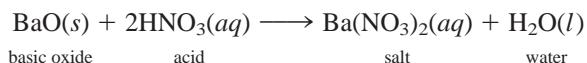
**Figure 16.8**  
Oxides of the representative elements in their highest oxidation states.

**Figure 16.9**

*Left: A beaker of water to which a few drops of bromothymol blue indicator have been added. Right: As dry ice is added to the water, the CO<sub>2</sub> reacts to form carbonic acid, which turns the solution acidic and changes the color from blue to yellow.*



Reactions between acidic oxides and bases and those between basic oxides and acids resemble normal acid-base reactions in that the products are a salt and water:



As Figure 16.8 shows, aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) is amphoteric. Depending on the reaction conditions, it can behave either as an acidic oxide or as a basic oxide. For example, Al<sub>2</sub>O<sub>3</sub> acts as a base with hydrochloric acid to produce a salt (AlCl<sub>3</sub>) and water:

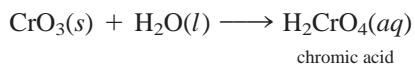
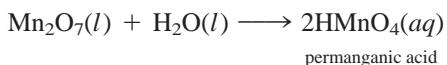


and acts as an acid with sodium hydroxide:



Note that only a salt, NaAl(OH)<sub>4</sub> [containing the Na<sup>+</sup> and Al(OH)<sub>4</sub><sup>-</sup> ions], is formed in the latter reaction; no water is produced. Nevertheless, this reaction can still be classified as an acid-base reaction because Al<sub>2</sub>O<sub>3</sub> neutralizes NaOH.

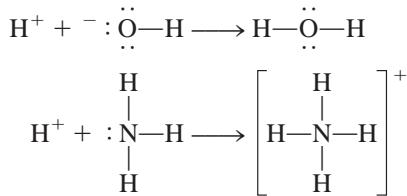
Some transition metal oxides in which the metal has a high oxidation number act as acidic oxides. Consider manganese(VII) oxide (Mn<sub>2</sub>O<sub>7</sub>) and chromium(VI) oxide (CrO<sub>3</sub>), both of which react with water to produce acids:



**The higher the oxidation number of the metal, the more covalent the compound; the lower the oxidation number, the more ionic the compound.**

## 16.11 Lewis Acids and Bases

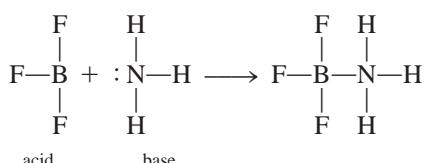
Acid-base properties so far have been discussed in terms of the Brønsted theory. To behave as a Brønsted base, for example, a substance must be able to accept protons. By this definition both the hydroxide ion and ammonia are bases:



In each case, the atom to which the proton becomes attached possesses at least one unshared pair of electrons. This characteristic property of the  $\text{OH}^-$  ion, of  $\text{NH}_3$ , and of other Brønsted bases suggests a more general definition of acids and bases.

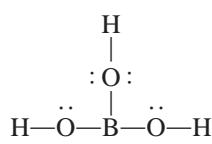
The American chemist G. N. Lewis formulated such a definition. According to Lewis's definition, a base is *a substance that can donate a pair of electrons*, and an acid is *a substance that can accept a pair of electrons*. For example, in the protonation of ammonia,  $\text{NH}_3$  acts as a **Lewis base** because it donates a pair of electrons to the proton  $\text{H}^+$ , which acts as a **Lewis acid** by accepting the pair of electrons. A Lewis acid-base reaction, therefore, is one that involves the donation of a pair of electrons from one species to another. Such a reaction does not produce a salt and water.

The significance of the Lewis concept is that it is much more general than other definitions; it includes as acid-base reactions many reactions that do not involve Brønsted acids. Consider, for example, the reaction between boron trifluoride ( $\text{BF}_3$ ) and ammonia (Figure 16.10):



In Section 10.4 we saw that the B atom in  $\text{BF}_3$  is  $sp^2$ -hybridized. The vacant, unhybridized  $2p_z$  orbital accepts the pair of electrons from  $\text{NH}_3$ . So  $\text{BF}_3$  functions as an acid according to the Lewis definition, even though it does not contain an ionizable proton. Note that a coordinate covalent bond is formed between the B and N atoms (see p. 299).

Another Lewis acid containing boron is boric acid ( $\text{H}_3\text{BO}_3$ ). Boric acid (a weak acid used in eyewash) is an oxoacid with the following structure:

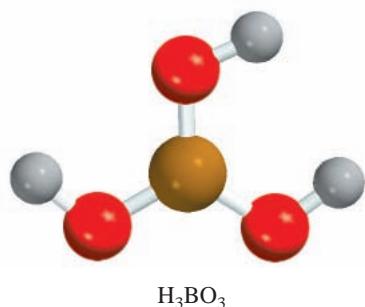


Note that boric acid does not ionize in water to produce an  $\text{H}^+$  ion. Instead, its reaction with water is



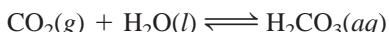
**Figure 16.10**  
A Lewis acid-base reaction involving  $\text{BF}_3$  and  $\text{NH}_3$ .

All Brønsted bases are Lewis bases.

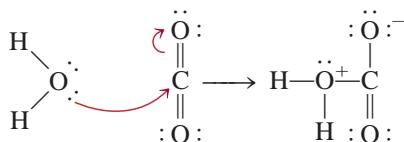


In this Lewis acid-base reaction, boric acid accepts a pair of electrons from the hydroxide ion that is derived from the H<sub>2</sub>O molecule.

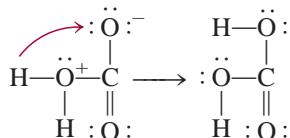
The hydration of carbon dioxide to produce carbonic acid



can be understood in the Lewis framework as follows: The first step involves donation of a lone pair on the oxygen atom in H<sub>2</sub>O to the carbon atom in CO<sub>2</sub>. An orbital is vacated on the C atom to accommodate the lone pair by removal of the electron pair in the C—O pi bond. These shifts of electrons are indicated by the curved arrows.



Therefore, H<sub>2</sub>O is a Lewis base and CO<sub>2</sub> is a Lewis acid. Next, a proton is transferred onto the O atom bearing a negative charge to form H<sub>2</sub>CO<sub>3</sub>.



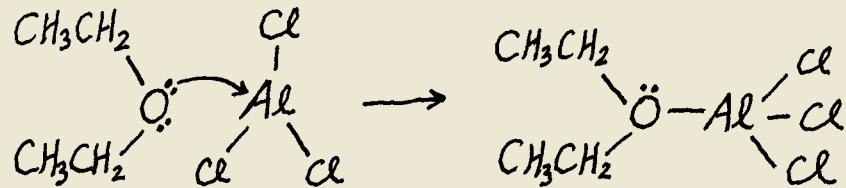
### Example 16.15

Identify the Lewis acid and Lewis base in each of the following reactions:

- (a) C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub> + AlCl<sub>3</sub>  $\rightleftharpoons$  (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>OAlCl<sub>3</sub>  
 (b) Hg<sup>2+</sup>(aq) + 4CN<sup>-</sup>(aq)  $\rightleftharpoons$  Hg(CN)<sub>4</sub><sup>2-</sup>(aq)

**Strategy** In Lewis acid-base reactions, the acid is usually a cation or an electron-deficient molecule, whereas the base is an anion or a molecule containing an atom with lone pairs.  
 (a) Draw the molecular structure for C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub>. What is the hybridization state of Al in AlCl<sub>3</sub>? (b) Which ion is likely to be an electron acceptor? An electron donor?

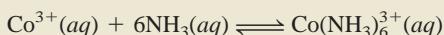
**Solution** (a) The Al is *sp*<sup>2</sup>-hybridized in AlCl<sub>3</sub> with an empty 2p<sub>z</sub> orbital. It is electron-deficient, sharing only six electrons. Therefore, the Al atom has a tendency to gain two electrons to complete its octet. This property makes AlCl<sub>3</sub> a Lewis acid. On the other hand, the lone pairs on the oxygen atom in C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub> make the compound a Lewis base:



- (b) Here the Hg<sup>2+</sup> ion accepts four pairs of electrons from the CN<sup>-</sup> ions. Therefore Hg<sup>2+</sup> is the Lewis acid and CN<sup>-</sup> is the Lewis base.

**Similar problem:** 16.80.

**Practice Exercise** Identify the Lewis acid and Lewis base in the reaction



## KEY EQUATIONS

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \quad (16.4)$$

$$pH = -\log [H^+] \quad (16.5)$$

$$[H^+] = 10^{-pH} \quad (16.6)$$

$$pOH = -\log [OH^-] \quad (16.8)$$

$$pH + pOH = 14.00 \quad (16.9)$$

$$\text{percent ionization} = \frac{\text{ionized acid concentration at equilibrium}}{\text{initial concentration of acid}} \times 100\% \quad (16.11)$$

$$K_a K_b = K_w \quad (16.12)$$

Relationship between the acid and base ionization constants of a conjugate acid-base pair.

## SUMMARY OF FACTS AND CONCEPTS

- Brønsted acids donate protons, and Brønsted bases accept protons. These are the definitions that normally underlie the use of the terms “acid” and “base.”
- The acidity of an aqueous solution is expressed as its pH, which is defined as the negative logarithm of the hydrogen ion concentration (in mol/L).
- At 25°C, an acidic solution has pH < 7, a basic solution has pH > 7, and a neutral solution has pH = 7.
- In aqueous solution, the following are classified as strong acids: HClO<sub>4</sub>, HI, HBr, HCl, H<sub>2</sub>SO<sub>4</sub> (first stage of ionization), and HNO<sub>3</sub>. Strong bases in aqueous solution include hydroxides of alkali metals and of alkaline earth metals (except beryllium).
- The acid ionization constant  $K_a$  increases with acid strength.  $K_b$  similarly expresses the strengths of bases.
- Percent ionization is another measure of the strength of acids. The more dilute a solution of a weak acid, the greater the percent ionization of the acid.
- The product of the ionization constant of an acid and the ionization constant of its conjugate base is equal to the ion-product constant of water.
- The relative strengths of acids can be explained qualitatively in terms of their molecular structures.
- Most salts are strong electrolytes that dissociate completely into ions in solution. The reaction of these ions with water, called salt hydrolysis, can produce acidic or basic solutions. In salt hydrolysis, the conjugate bases of weak acids yield basic solutions, and the conjugate acids of weak bases yield acidic solutions.
- Small, highly charged metal ions, such as Al<sup>3+</sup> and Fe<sup>3+</sup>, hydrolyze to yield acidic solutions.
- Most oxides can be classified as acidic, basic, or amphoteric. Metal hydroxides are either basic or amphoteric.
- Lewis acids accept pairs of electrons and Lewis bases donate pairs of electrons. The term “Lewis acid” is generally reserved for substances that can accept electron pairs but do not contain ionizable hydrogen atoms.

## KEY WORDS

Acid ionization constant ( $K_a$ ),  
p. 540

Base ionization constant ( $K_b$ ),  
p. 551

Conjugate acid-base pair,  
p. 530

Ion-product constant, p. 532  
Lewis acid, p. 565

Lewis base, p. 565

Percent ionization, p. 546

pH, p. 533

Salt hydrolysis, p. 557

Strong acid, p. 536

Strong base, p. 536

Weak acid, p. 536

Weak base, p. 537

## QUESTIONS AND PROBLEMS

### Brønsted Acids and Bases

#### Review Questions

- 16.1 Define Brønsted acids and bases. How do the Brønsted definitions differ from Arrhenius's definitions of acids and bases?
- 16.2 For a species to act as a Brønsted base, an atom in the species must possess a lone pair of electrons. Explain why this is so.

#### Problems

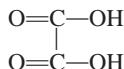
- 16.3 Classify each of these species as a Brønsted acid or base, or both: (a) H<sub>2</sub>O, (b) OH<sup>-</sup>, (c) H<sub>3</sub>O<sup>+</sup>, (d) NH<sub>3</sub>, (e) NH<sub>4</sub><sup>+</sup>, (f) NH<sub>2</sub><sup>-</sup>, (g) NO<sub>3</sub><sup>-</sup>, (h) CO<sub>3</sub><sup>2-</sup>, (i) HBr, (j) HCN.
- 16.4** What are the names and formulas of the conjugate bases of these acids: (a) HNO<sub>2</sub>, (b) H<sub>2</sub>SO<sub>4</sub>, (c) H<sub>2</sub>S, (d) HCN, (e) HCOOH (formic acid)?

- 16.5 Identify the acid-base conjugate pairs in each of these reactions:
- (a) CH<sub>3</sub>COO<sup>-</sup> + HCN  $\rightleftharpoons$  CH<sub>3</sub>COOH + CN<sup>-</sup>
- (b) HCO<sub>3</sub><sup>-</sup> + HCO<sub>3</sub><sup>-</sup>  $\rightleftharpoons$  H<sub>2</sub>CO<sub>3</sub> + CO<sub>3</sub><sup>2-</sup>
- (c) H<sub>2</sub>PO<sub>4</sub><sup>-</sup> + NH<sub>3</sub>  $\rightleftharpoons$  HPO<sub>4</sub><sup>2-</sup> + NH<sub>4</sub><sup>+</sup>
- (d) HClO + CH<sub>3</sub>NH<sub>2</sub>  $\rightleftharpoons$  CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> + ClO<sup>-</sup>
- (e) CO<sub>3</sub><sup>2-</sup> + H<sub>2</sub>O  $\rightleftharpoons$  HCO<sub>3</sub><sup>-</sup> + OH<sup>-</sup>
- (f) CH<sub>3</sub>COO<sup>-</sup> + H<sub>2</sub>O  $\rightleftharpoons$  CH<sub>3</sub>COOH + OH<sup>-</sup>

- 16.6** Give the conjugate acid of each of these bases: (a) HS<sup>-</sup>, (b) HCO<sub>3</sub><sup>-</sup>, (c) CO<sub>3</sub><sup>2-</sup>, (d) H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, (e) HPO<sub>4</sub><sup>2-</sup>, (f) PO<sub>4</sub><sup>3-</sup>, (g) HSO<sub>4</sub><sup>-</sup>, (h) SO<sub>4</sub><sup>2-</sup>, (i) NO<sub>2</sub><sup>-</sup>, (j) SO<sub>3</sub><sup>2-</sup>.

- 16.7 Give the conjugate base of each of these acids: (a) CH<sub>2</sub>ClCOOH, (b) HIO<sub>4</sub>, (c) H<sub>3</sub>PO<sub>4</sub>, (d) H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, (e) HPO<sub>4</sub><sup>2-</sup>, (f) H<sub>2</sub>SO<sub>4</sub>, (g) HSO<sub>4</sub><sup>-</sup>, (h) HCOOH, (i) HSO<sub>3</sub><sup>-</sup>, (j) NH<sub>4</sub><sup>+</sup>, (k) H<sub>2</sub>S, (l) HS<sup>-</sup>, (m) HClO.

- 16.8** Oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) has the following structure:



An oxalic acid solution contains these species in varying concentrations: H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, HC<sub>2</sub>O<sub>4</sub><sup>-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, and H<sup>+</sup>. (a) Draw Lewis structures of HC<sub>2</sub>O<sub>4</sub><sup>-</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup>. (b) Which of the four species listed here can act only as acids, which can act only as bases, and which can act as both acids and bases?

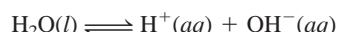
### pH and pOH Calculations

#### Review Questions

- 16.9 What is the ion-product constant for water?

- 16.10 Write an equation relating [H<sup>+</sup>] and [OH<sup>-</sup>] in solution at 25°C.

- 16.11 The ion-product constant for water is  $1.0 \times 10^{-14}$  at 25°C and  $3.8 \times 10^{-14}$  at 40°C. Is the process



endothermic or exothermic?

- 16.12 Define pH. Why do chemists normally choose to discuss the acidity of a solution in terms of pH rather than hydrogen ion concentration, [H<sup>+</sup>]?

- 16.13 The pH of a solution is 6.7. From this statement alone, can you conclude that the solution is acidic? If not, what additional information would you need? Can the pH of a solution be zero or negative? If so, give examples to illustrate these values.

- 16.14 Define pOH. Write an equation relating pH and pOH.

#### Problems

- 16.15 Calculate the hydrogen ion concentration for solutions with these pH values: (a) 2.42, (b) 11.21, (c) 6.96, (d) 15.00.

- 16.16** Calculate the hydrogen ion concentration in moles per liter for each of these solutions: (a) a solution whose pH is 5.20, (b) a solution whose pH is 16.00; (c) a solution whose hydroxide concentration is  $3.7 \times 10^{-9} M$ .

- 16.17 Calculate the pH of each of these solutions: (a) 0.0010 M HCl, (b) 0.76 M KOH, (c)  $2.8 \times 10^{-4} M$  Ba(OH)<sub>2</sub>, (d)  $5.2 \times 10^{-4} M$  HNO<sub>3</sub>.

- 16.18** Calculate the pH of water at 40°C, given that K<sub>w</sub> is  $3.8 \times 10^{-14}$  at this temperature.

- 16.19 Complete this table for a solution:

| pH  | [H <sup>+</sup> ]        | Solution is |
|-----|--------------------------|-------------|
| < 7 |                          |             |
|     | $< 1.0 \times 10^{-7} M$ |             |
|     |                          | Neutral     |

- 16.20** Fill in the word "acidic," "basic," or "neutral" for these solutions:

- (a) pOH > 7; solution is \_\_\_\_\_.

- (b) pOH = 7; solution is \_\_\_\_\_.

- (c) pOH < 7; solution is \_\_\_\_\_.

- 16.21 The pOH of a solution is 9.40. Calculate the hydrogen ion concentration of the solution.

- 16.22** Calculate the number of moles of KOH in 5.50 mL of a 0.360 M KOH solution. What is the pOH of the solution?

- 16.23 A solution is made by dissolving 18.4 g of HCl in 662 mL of water. Calculate the pH of the solution. (Assume that the volume of the solution is also 662 mL.)
- 16.24** How much NaOH (in grams) is needed to prepare 546 mL of solution with a pH of 10.00?

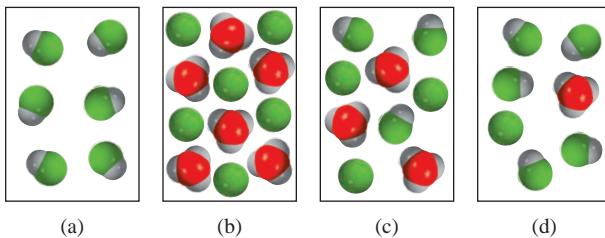
## Strengths of Acids and Bases

### Review Questions

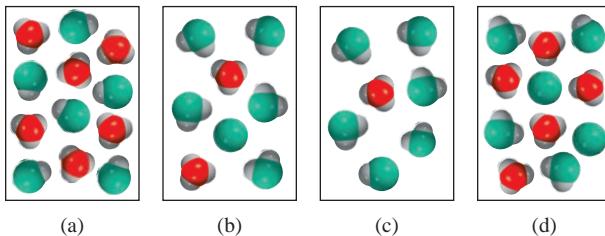
- 16.25 Explain what is meant by the strength of an acid.
- 16.26 Without referring to the text, write the formulas of four strong acids and four weak acids.
- 16.27 What are the strongest acid and strongest base that can exist in water?
- 16.28  $\text{H}_2\text{SO}_4$  is a strong acid, but  $\text{HSO}_4^-$  is a weak acid. Account for the difference in strength of these two related species.

### Problems

- 16.29 Which of the following diagrams best represents a strong acid, such as HCl, dissolved in water? Which represents a weak acid? Which represents a very weak acid? (The hydrated proton is shown as a hydronium ion. Water molecules are omitted for clarity.)



- 16.30** (1) Which of the following diagrams represents a solution of a weak diprotic acid? (2) Which diagrams represent chemically implausible situations? (The hydrated proton is shown as a hydronium ion. Water molecules are omitted for clarity.)



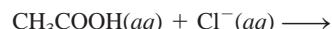
- 16.31 Classify each of these species as a weak or strong acid: (a)  $\text{HNO}_3$ , (b) HF, (c)  $\text{H}_2\text{SO}_4$ , (d)  $\text{HSO}_4^-$ , (e)  $\text{H}_2\text{CO}_3$ , (f)  $\text{HCO}_3^-$ , (g) HCl, (h) HCN, (i)  $\text{HNO}_2$ .
- 16.32** Classify each of these species as a weak or strong base: (a) LiOH, (b)  $\text{CN}^-$ , (c)  $\text{H}_2\text{O}$ , (d)  $\text{ClO}_4^-$ , (e)  $\text{NH}_2^-$ .

- 16.33 Which of these statements is/are true regarding a 0.10 M solution of a weak acid HA?
- The pH is 1.00.
  - $[\text{H}^+] \gg [\text{A}^-]$
  - $[\text{H}^+] = [\text{A}^-]$
  - The pH is less than 1.

- 16.34** Which of these statements is/are true regarding a 1.0 M solution of a strong acid HA?
- $[\text{A}^-] > [\text{H}^+]$
  - The pH is 0.00.
  - $[\text{H}^+] = 1.0 \text{ M}$
  - $[\text{HA}] = 1.0 \text{ M}$

- 16.35 Predict the direction that predominates in this reaction:
- $$\text{F}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HF}(aq) + \text{OH}^-(aq)$$

- 16.36** Predict whether this reaction will proceed from left to right to any measurable extent:



## Weak Acid Ionization Constants

### Review Questions

- 16.37 What does the ionization constant tell us about the strength of an acid?
- 16.38 List the factors on which the  $K_a$  of a weak acid depends.
- 16.39 Why do we normally not quote  $K_a$  values for strong acids such as HCl and  $\text{HNO}_3$ ? Why is it necessary to specify temperature when giving  $K_a$  values?
- 16.40 Which of the following solutions has the highest pH? (a) 0.40 M  $\text{HCOOH}$ , (b) 0.40 M  $\text{HClO}_4$ , (c) 0.40 M  $\text{CH}_3\text{COOH}$ .

### Problems

- 16.41 Calculate the concentrations of all the species ( $\text{HCN}$ ,  $\text{H}^+$ ,  $\text{CN}^-$ , and  $\text{OH}^-$ ) in a 0.15 M HCN solution.
- 16.42** A 0.0560-g quantity of acetic acid is dissolved in enough water to make 50.0 mL of solution. Calculate the concentrations of  $\text{H}^+$ ,  $\text{CH}_3\text{COO}^-$ , and  $\text{CH}_3\text{COOH}$  at equilibrium. ( $K_a$  for acetic acid =  $1.8 \times 10^{-5}$ .)
- 16.43 The pH of an HF solution is 6.20. Calculate the ratio  $[\text{conjugate base}]/[\text{acid}]$  for HF at this pH.
- 16.44** What is the original molarity of a solution of formic acid ( $\text{HCOOH}$ ) whose pH is 3.26 at equilibrium?
- 16.45 Calculate the pH of a 0.060 M HF solution.
- 16.46** Calculate the percent ionization of hydrofluoric acid at these concentrations: (a) 0.60 M, (b) 0.080 M, (c) 0.0046 M, (d) 0.00028 M. Comment on the trends.

- 16.47 A 0.040  $M$  solution of a monoprotic acid is 14 percent ionized. Calculate the ionization constant of the acid.

- 16.48** (a) Calculate the percent ionization of a 0.20  $M$  solution of the monoprotic acetylsalicylic acid (aspirin). ( $K_a = 3.0 \times 10^{-4}$ .) (b) The pH of gastric juice in the stomach of a certain individual is 1.00. After a few aspirin tablets have been swallowed, the concentration of acetylsalicylic acid in the stomach is 0.20  $M$ . Calculate the percent ionization of the acid under these conditions.

## Diprotic and Polyprotic Acids

### Review Questions

- 16.49 Malonic acid  $[\text{CH}_2(\text{COOH})_2]$  is a diprotic acid. Explain what that means.
- 16.50 Write all the species (except water) that are present in a phosphoric acid solution. Indicate which species can act as a Brønsted acid, which as a Brønsted base, and which as both a Brønsted acid and a Brønsted base.

### Problems

- 16.51 What are the concentrations of  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}^+$  in a 0.20  $M$   $\text{KHSO}_4$  solution? (Hint:  $\text{H}_2\text{SO}_4$  is a strong acid:  $K_a$  for  $\text{HSO}_4^- = 1.3 \times 10^{-2}$ .)
- 16.52** Calculate the concentrations of  $\text{H}^+$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  in a 0.025  $M$   $\text{H}_2\text{CO}_3$  solution.

## Weak Base Ionization Constants; $K_a$ – $K_b$ Relationship

### Review Questions

- 16.53 Use  $\text{NH}_3$  to illustrate what we mean by the strength of a base.
- 16.54 Write the equation relating  $K_a$  for a weak acid and  $K_b$  for its conjugate base. Use  $\text{NH}_3$  and its conjugate acid  $\text{NH}_4^+$  to derive the relationship between  $K_a$  and  $K_b$ .

### Problems

- 16.55 Calculate the pH for each of these solutions: (a) 0.10  $M$   $\text{NH}_3$ , (b) 0.050  $M$  pyridine.
- 16.56** The pH of a 0.30  $M$  solution of a weak base is 10.66. What is the  $K_b$  of the base?
- 16.57 What is the original molarity of a solution of ammonia whose pH is 11.22?
- 16.58** In a 0.080  $M$   $\text{NH}_3$  solution, what percent of the  $\text{NH}_3$  is present as  $\text{NH}_4^+$ ?

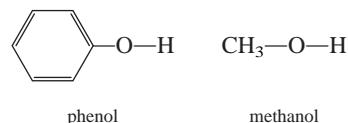
## Molecular Structure and the Strength of Acids

### Review Questions

- 16.59 List four factors that affect the strength of an acid.
- 16.60 How does the strength of an oxoacid depend on the electronegativity and oxidation number of the central atom?

## Problems

- 16.61 Predict the acid strengths of the following compounds:  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ , and  $\text{H}_2\text{Se}$ .
- 16.62** Compare the strengths of the following pairs of acids: (a)  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{SeO}_4$ , (b)  $\text{H}_3\text{PO}_4$  and  $\text{H}_3\text{AsO}_4$ .
- 16.63 Which of the following is the stronger acid:  $\text{CH}_2\text{ClCOOH}$  or  $\text{CHCl}_2\text{COOH}$ ? Explain your choice.
- 16.64** Consider the following compounds:



Experimentally, phenol is found to be a stronger acid than methanol. Explain this difference in terms of the structures of the conjugate bases. (Hint: A more stable conjugate base favors ionization. Only one of the conjugate bases can be stabilized by resonance.)

## Acid-Base Properties of Salt Solutions

### Review Questions

- 16.65 Define salt hydrolysis. Categorize salts according to how they affect the pH of a solution.
- 16.66 Explain why small, highly charged metal ions are able to undergo hydrolysis.
- 16.67  $\text{Al}^{3+}$  is not a Brønsted acid, but  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  is. Explain.
- 16.68 Specify which of these salts will undergo hydrolysis:  $\text{KF}$ ,  $\text{NaNO}_3$ ,  $\text{NH}_4\text{NO}_2$ ,  $\text{MgSO}_4$ ,  $\text{KCN}$ ,  $\text{C}_6\text{H}_5\text{COONa}$ ,  $\text{RbI}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCl}_2$ ,  $\text{HCOK}$ .
- 16.69 Predict the pH ( $>7$ ,  $<7$ , or  $\approx 7$ ) of the aqueous solutions containing the following salts: (a)  $\text{KBr}$ , (b)  $\text{Al}(\text{NO}_3)_3$ , (c)  $\text{BaCl}_2$ , (d)  $\text{Bi}(\text{NO}_3)_3$ .
- 16.70 Which ion of the alkaline earth metals is most likely to undergo hydrolysis?

### Problems

- 16.71 A certain salt,  $\text{MX}$  (containing the  $\text{M}^+$  and  $\text{X}^-$  ions), is dissolved in water, and the pH of the resulting solution is 7.0. Can you say anything about the strengths of the acid and the base from which the salt is derived?
- 16.72** In a certain experiment a student finds that the pHs of 0.10  $M$  solutions of three potassium salts  $\text{KX}$ ,  $\text{KY}$ , and  $\text{KZ}$  are 7.0, 9.0, and 11.0, respectively. Arrange the acids  $\text{HX}$ ,  $\text{HY}$ , and  $\text{HZ}$  in order of increasing acid strength.
- 16.73 Calculate the pH of a 0.36  $M$   $\text{CH}_3\text{COONa}$  solution.
- 16.74** Calculate the pH of a 0.42  $M$   $\text{NH}_4\text{Cl}$  solution.

- 16.75 Predict whether a solution containing the salt  $\text{K}_2\text{HPO}_4$  will be acidic, neutral, or basic. (*Hint:* You need to consider both the ionization and hydrolysis of  $\text{HPO}_4^{2-}$ .)

- 16.76** Predict the pH ( $>7$ ,  $<7$ ,  $\approx 7$ ) of a  $\text{NaHCO}_3$  solution.

## Lewis Acids and Bases

### Review Questions

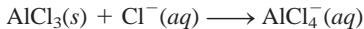
- 16.77 What are the Lewis definitions of an acid and a base? In what way are they more general than the Brønsted definitions?

- 16.78 In terms of orbitals and electron arrangements, what must be present for a molecule or an ion to act as a Lewis acid (use  $\text{H}^+$  and  $\text{BF}_3$  as examples)? What must be present for a molecule or ion to act as a Lewis base (use  $\text{OH}^-$  and  $\text{NH}_3$  as examples)?

### Problems

- 16.79 Classify each of these following species as a Lewis acid or a Lewis base: (a)  $\text{CO}_2$ , (b)  $\text{H}_2\text{O}$ , (c)  $\text{I}^-$ , (d)  $\text{SO}_2$ , (e)  $\text{NH}_3$ , (f)  $\text{OH}^-$ , (g)  $\text{H}^+$ , (h)  $\text{BCl}_3$ .

- 16.80** Describe this reaction according to the Lewis theory of acids and bases:



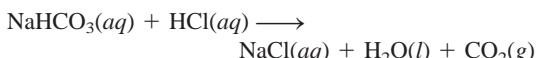
- 16.81 Which would be considered a stronger Lewis acid: (a)  $\text{BF}_3$  or  $\text{BCl}_3$ , (b)  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ? Explain.

- 16.82** All Brønsted acids are Lewis acids, but the reverse is not true. Give two examples of Lewis acids that are not Brønsted acids.

## Additional Problems

- 16.83 Classify these following oxides as acidic, basic, amphoteric, or neutral: (a)  $\text{CO}_2$ , (b)  $\text{K}_2\text{O}$ , (c)  $\text{CaO}$ , (d)  $\text{N}_2\text{O}_5$ , (e)  $\text{CO}$ , (f)  $\text{NO}$ , (g)  $\text{SnO}_2$ , (h)  $\text{SO}_3$ , (i)  $\text{Al}_2\text{O}_3$ , (j)  $\text{BaO}$ .

- 16.84** A typical reaction between an antacid and the hydrochloric acid in gastric juice is



Calculate the volume (in liters) of  $\text{CO}_2$  generated from 0.350 g of  $\text{NaHCO}_3$  and excess gastric juice at 1.00 atm and  $37.0^\circ\text{C}$ .

- 16.85 To which of the following would the addition of an equal volume of 0.60 M  $\text{NaOH}$  lead to a solution having a lower pH? (a) water, (b) 0.30 M  $\text{HCl}$ , (c) 0.70 M  $\text{KOH}$ , (d) 0.40 M  $\text{NaNO}_3$ .

- 16.86** The pH of a 0.0642 M solution of a monoprotic acid is 3.86. Is this a strong acid?

- 16.87 Like water, ammonia undergoes autoionization in liquid ammonia:



- (a) Identify the Brønsted acids and Brønsted bases in this reaction. (b) What species correspond to  $\text{H}^+$  and  $\text{OH}^-$ , and what is the condition for a neutral solution?

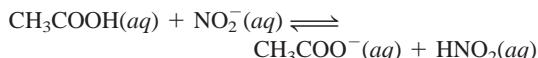
- 16.88** HA and HB are both weak acids although HB is the stronger of the two. Will it take more volume of a 0.10 M  $\text{NaOH}$  solution to neutralize 50.0 mL of 0.10 M HB than 50.0 mL of 0.10 M HA?

- 16.89 A 1.87-g sample of Mg reacts with 80.0 mL of a HCl solution whose pH is  $-0.544$ . What is the pH of the solution after all the Mg has reacted? Assume volume of solution is constant.

- 16.90** The three common chromium oxides are  $\text{CrO}$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{CrO}_3$ . If  $\text{Cr}_2\text{O}_3$  is amphoteric, what can you say about the acid-base properties of  $\text{CrO}$  and  $\text{CrO}_3$ ?

- 16.91 Most of the hydrides of Group 1A and Group 2A metals are ionic (the exceptions are  $\text{BeH}_2$  and  $\text{MgH}_2$ , which are covalent compounds). (a) Describe the reaction between the hydride ion ( $\text{H}^-$ ) and water in terms of a Brønsted acid-base reaction. (b) The same reaction can also be classified as a redox reaction. Identify the oxidizing and reducing agents.

- 16.92** Use the data in Table 16.3 to calculate the equilibrium constant for the following reaction:



- 16.93 Calculate the pH of a 0.20 M ammonium acetate ( $\text{CH}_3\text{COONH}_4$ ) solution.

- 16.94** Novocaine, used as a local anesthetic by dentists, is a weak base ( $K_b = 8.91 \times 10^{-6}$ ). What is the ratio of the concentration of the base to that of its acid in the blood plasma (pH = 7.40) of a patient?

- 16.95 In the vapor phase, acetic acid molecules associate to a certain extent to form dimers:



At  $51^\circ\text{C}$ , the pressure of a certain acetic acid vapor system is 0.0342 atm in a 360-mL flask. The vapor is condensed and neutralized with 13.8 mL of 0.0568 M  $\text{NaOH}$ . (a) Calculate the degree of dissociation ( $\alpha$ ) of the dimer under these conditions:



(*Hint:* See Problem 15.65 for general procedure.) (b) Calculate the equilibrium constant  $K_P$  for the reaction in (a).

- 16.96** Calculate the concentrations of all the species in a 0.100 M  $\text{Na}_2\text{CO}_3$  solution.

- 16.97 Henry's law constant for  $\text{CO}_2$  at  $38^\circ\text{C}$  is  $2.28 \times 10^{-3}$  mol/L · atm. Calculate the pH of a solution of  $\text{CO}_2$  at  $38^\circ\text{C}$  in equilibrium with the gas at a partial pressure of 3.20 atm.

- 16.98** Hydrocyanic acid (HCN) is a weak acid and a deadly poisonous compound that, in the gaseous form (hydrogen cyanide), is used in gas chambers. Why is it dangerous to treat sodium cyanide with acids (such as HCl) without proper ventilation?
- 16.99 A solution of formic acid ( $\text{HCOOH}$ ) has a pH of 2.53. How many grams of formic acid are there in 100.0 mL of the solution?
- 16.100** Calculate the pH of a 1-L solution containing 0.150 mole of  $\text{CH}_3\text{COOH}$  and 0.100 mole of HCl.
- 16.101 You are given two beakers containing separately an aqueous solution of strong acid (HA) and an aqueous solution of weak acid (HB) of the same concentration. Describe how you would compare the strengths of these two acids by (a) measuring the pH, (b) measuring electrical conductance, (c) studying the rate of hydrogen gas evolution when these solutions are reacted with an active metal such as Mg or Zn.
- 16.102** Use Le Châtelier's principle to predict the effect of the following changes on the extent of hydrolysis of sodium nitrite ( $\text{NaNO}_2$ ) solution: (a) HCl is added; (b) NaOH is added; (c) NaCl is added; (d) the solution is diluted.
- 16.103 The disagreeable odor of fish is mainly due to organic compounds ( $\text{RNH}_2$ ) containing an amino group,  $-\text{NH}_2$ , in which R is the rest of the molecule. Amines are bases just like ammonia. Explain why putting some lemon juice on fish can greatly reduce the odor.
- 16.104** A 0.400 M formic acid ( $\text{HCOOH}$ ) solution freezes at  $-0.758^\circ\text{C}$ . Calculate the  $K_a$  of the acid at that temperature. (Hint: Assume that molarity is equal to molality. Carry your calculations to three significant figures and round off to two for  $K_a$ .)
- 16.105 Both the amide ion ( $\text{NH}_2^-$ ) and the nitride ion ( $\text{N}^{3-}$ ) are stronger bases than the hydroxide ion and hence do not exist in aqueous solutions. (a) Write the equations showing the reactions of these ions with water, and identify the Brønsted acid and base in each case. (b) Which of the two is the stronger base?
- 16.106** The atmospheric sulfur dioxide ( $\text{SO}_2$ ) concentration over a certain region is 0.12 ppm by volume. Calculate the pH of the rainwater as a result of this pollutant. Assume that the dissolution of  $\text{SO}_2$  does not affect its pressure and that the pH of rainwater is solely due to this compound.
- 16.107 Explain the action of smelling salt, which is ammonium carbonate  $[(\text{NH}_4)_2\text{CO}_3]$ . (Hint: The thin film of aqueous solution that lines the nasal passage is slightly basic.)
- 16.108** Which of the following is the stronger base:  $\text{NF}_3$  or  $\text{NH}_3$ ? (Hint: F is more electronegative than H.)
- 16.109 Which of the following is a stronger base:  $\text{NH}_3$  or  $\text{PH}_3$ ? (Hint: The N—H bond is stronger than the P—H bond.)
- 16.110** How many milliliters of a strong monoprotic acid solution at pH = 4.12 must be added to 528 mL of the same acid solution at pH = 5.76 to change its pH to 5.34? Assume that the volumes are additive.
- 16.111 When chlorine reacts with water, the resulting solution is weakly acidic and reacts with  $\text{AgNO}_3$  to give a white precipitate. Write balanced equations to represent these reactions. Explain why manufacturers of household bleaches add bases such as NaOH to their products to increase their effectiveness.
- 16.112** Calculate the concentrations of all species in a 0.100 M  $\text{H}_3\text{PO}_4$  solution.
- 16.113 A solution of methylamine ( $\text{CH}_3\text{NH}_2$ ) has a pH of 10.64. How many grams of methylamine are there in 100.0 mL of the solution?

## SPECIAL PROBLEMS

**16.114** About half of the hydrochloric acid produced annually in the United States (3.0 billion pounds) is used for metal pickling. This process involves the removal of metal oxide layers from metal surfaces to prepare them for coating. (a) Write the overall and net ionic equations for the reaction between iron(III) oxide, which represents the rust layer over iron, and HCl. Identify the Brønsted acid and base. (b) Hydrochloric acid is also used to remove scale (which is mostly  $\text{CaCO}_3$ ) from water pipes. Hydrochloric acid reacts with calcium carbonate in two stages; the first stage forms the bicarbonate ion, which then reacts further to form carbon dioxide. Write equations for these two stages and for the overall reaction.

(c) Hydrochloric acid is used to recover oil from the ground. It dissolves rocks (often  $\text{CaCO}_3$ ) so that the oil can flow more easily. In one process, a 15 percent (by mass) HCl solution is injected into an oil well to dissolve the rocks. If the density of the acid solution is 1.073 g/mL, what is the pH of the solution?

**16.115** Hemoglobin (Hb) is a blood protein that is responsible for transporting oxygen. It can exist in the protonated form of  $\text{HbH}^+$ . The binding of oxygen can be represented by the simplified equation



(a) What form of hemoglobin is favored in the lungs where oxygen concentration is highest? (b) In body

tissues, where carbon dioxide is released as a result of metabolism, the medium is more acidic because of the formation of carbonic acid. What form of hemoglobin is favored under this condition? (c) When a person hyperventilates, the concentration of  $\text{CO}_2$  in his or her blood decreases. How does this action affect the above equilibrium? Frequently a person who is hyperventilating is advised to breathe into a paper bag. Why does this action help the individual?

**16.116** A 1.294-g sample of a metal carbonate ( $\text{MCO}_3$ ) is reacted with 500 mL of a 0.100  $M$  HCl solution. The excess HCl acid is then neutralized by 32.80 mL of 0.588  $M$  NaOH. Identify M.

**16.117** Prove the statement that when the concentration of a weak acid HA decreases by a factor of 10, its percent ionization increases by a factor of  $\sqrt{10}$ . State any assumptions.

**16.118** Calculate the pH of a solution that is 1.00  $M$  HCN and 1.00  $M$  HF. Compare the concentration (in

molarity) of the  $\text{CN}^-$  ion in this solution with that in a 1.00  $M$  HCN solution. Comment on the difference.

**16.119** Teeth enamel is largely hydroxyapatite  $[\text{Ca}_5(\text{PO}_4)_3\text{OH}]$ . When it dissolves in water (a process called demineralization), it dissociates as follows:



The reverse process, called *remineralization*, is the body's natural defense against tooth decay. Acids produced from food remove the  $\text{OH}^-$  ions and thereby weaken the enamel layer. Most toothpastes contain a fluoride compound such as  $\text{NaF}$  or  $\text{SnF}_2$ . What is the function of these compounds in preventing tooth decay?

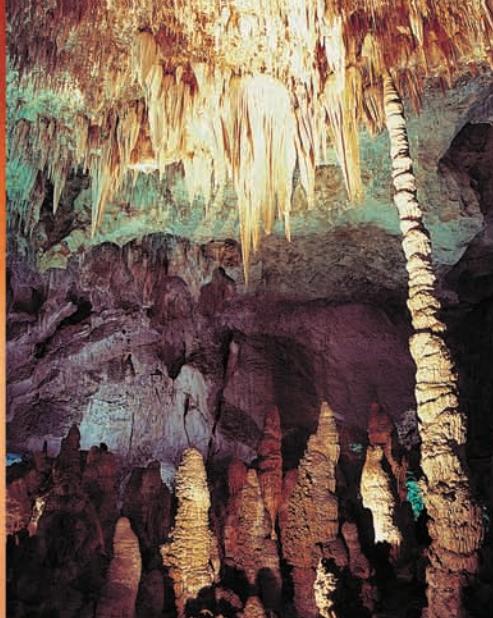
**16.120** Use the van't Hoff equation (see Problem 15.98) and the data in Appendix 2 to calculate the pH of water at its normal boiling point.

## ANSWERS TO PRACTICE EXERCISES

**16.1** (1)  $\text{H}_2\text{O}$  (acid) and  $\text{OH}^-$  (base); (2) HCN (acid) and  $\text{CN}^-$  (base). **16.2**  $7.7 \times 10^{-15} M$ . **16.3** 0.12. **16.4**  $4.7 \times 10^{-4} M$ . **16.5** 7.40. **16.6** 12.56. **16.7** Smaller than 1. **16.8** 2.09. **16.9**  $2.2 \times 10^{-6}$ . **16.10**  $[\text{H}_2\text{C}_2\text{O}_4] = 0.11 M$ ,

$[\text{HC}_2\text{O}_4^-] = 0.086 M$ ,  $[\text{C}_2\text{O}_4^{2-}] = 6.1 \times 10^{-5} M$ ,  $[\text{H}^+] = 0.086 M$ . **16.11** 12.03. **16.12**  $\text{HClO}_2$ .

**16.13** 8.58. **16.14** (a)  $\text{pH} \approx 7$ , (b)  $\text{pH} > 7$ , (c)  $\text{pH} < 7$ , (d)  $\text{pH} > 7$ . **16.15** Lewis acid:  $\text{Co}^{3+}$ ; Lewis base:  $\text{NH}_3$ .



Downward-growing, icicle-like stalactites and upward-growing columnar stalagmites.

## Acid-Base Equilibria and Solubility Equilibria

### CHAPTER OUTLINE

- 17.1** Homogeneous Versus Heterogeneous Solution Equilibria 575
- 17.2** Buffer Solutions 575  
Preparing a Buffer Solution with a Specific pH
- 17.3** A Closer Look at Acid-Base Titrations 580
  - Strong Acid–Strong Base Titrations •
  - Weak Acid–Strong Base Titrations •
  - Strong Acid–Weak Base Titrations
- 17.4** Acid-Base Indicators 586
- 17.5** Solubility Equilibria 589
  - Solubility Product • Molar Solubility and Solubility • Predicting Precipitation Reactions
- 17.6** The Common Ion Effect and Solubility 596
- 17.7** Complex Ion Equilibria and Solubility 597
- 17.8** Application of the Solubility Product Principle to Qualitative Analysis 600

### ESSENTIAL CONCEPTS

**Buffer Solutions** A buffer solution contains a weak acid and a salt derived from the acid. To maintain a relatively constant pH, the acid and base components of the buffer solution react with added acid or base. Buffer solutions play an important role in many chemical and biological processes.

**Acid-Base Titrations** The characteristics of an acid-base titration depend on the strength of the acid and base involved. Different indicators are used to determine the end point of a titration.

**Solubility Equilibria** Another application of the equilibrium concept is the solubility equilibria of sparingly soluble salts, which are expressed as the solubility product. The solubility of such a substance can be affected by the presence of a common cation or anion, or the pH. Complex-ion formation, an example of the Lewis acid-base type reaction, increases the solubility of an insoluble salt.



- 1. Animation: Buffer Solutions (17.2)
- 2. Animation: Acid-Base Titrations (17.3)

- 3. Interactivity: Neutralization Reaction I & II (17.3)

## 17.1 Homogeneous Versus Heterogeneous Solution Equilibria

In Chapter 16 we saw that weak acids and weak bases never ionize completely in water. Thus, at equilibrium a weak acid solution, for example, contains nonionized acid as well as  $\text{H}^+$  ions and the conjugate base. Nevertheless, all of these species are dissolved, so that the system is an example of homogeneous equilibrium (see Chapter 15).

Another important type of equilibrium, which we will study in the second half of the chapter, involves the dissolution and precipitation of slightly soluble substances. These processes are examples of heterogeneous equilibria; that is, they pertain to reactions in which the components are in more than one phase. But first we will conclude our discussion of acid-base equilibria by considering buffer solutions and taking a closer look at acid-base titrations.

## 17.2 Buffer Solutions

A **buffer solution** is a solution of (1) a weak acid or a weak base and (2) its salt; both components must be present. The solution has the ability to resist changes in pH upon the addition of small amounts of either acid or base. Buffers are very important to chemical and biological systems. The pH in the human body varies greatly from one fluid to another; for example, the pH of blood is about 7.4, whereas the gastric juice in our stomachs has a pH of about 1.5. These pH values, which are crucial for the proper functioning of enzymes and the balance of osmotic pressure, are maintained by buffers in most cases.

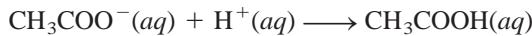
A buffer solution must contain a relatively large concentration of acid to react with any  $\text{OH}^-$  ions that may be added to it and must contain a similar concentration of base to react with any added  $\text{H}^+$  ions. Furthermore, the acid and the base components of the buffer must not consume each other in a neutralization reaction. These requirements are satisfied by an acid-base conjugate pair (a weak acid and its conjugate base or a weak base and its conjugate acid).

A simple buffer solution can be prepared by adding comparable amounts of acetic acid ( $\text{CH}_3\text{COOH}$ ) and sodium acetate ( $\text{CH}_3\text{COONa}$ ) to water. The equilibrium concentrations of both the acid and the conjugate base (from  $\text{CH}_3\text{COONa}$ ) are assumed to be the same as the starting concentrations. This is so because (1)  $\text{CH}_3\text{COOH}$  is a weak acid and the extent of hydrolysis of the  $\text{CH}_3\text{COO}^-$  ion is very small and (2) the presence of  $\text{CH}_3\text{COO}^-$  ions suppresses the ionization of  $\text{CH}_3\text{COOH}$ , and the presence of  $\text{CH}_3\text{COOH}$  suppresses the hydrolysis of the  $\text{CH}_3\text{COO}^-$  ions.

A solution containing these two substances has the ability to neutralize either added acid or added base. Sodium acetate, a strong electrolyte, dissociates completely in water:



If an acid is added, the  $\text{H}^+$  ions will be consumed by the conjugate base in the buffer,  $\text{CH}_3\text{COO}^-$ , according to the equation



If a base is added to the buffer system, the  $\text{OH}^-$  ions will be neutralized by the acid in the buffer:

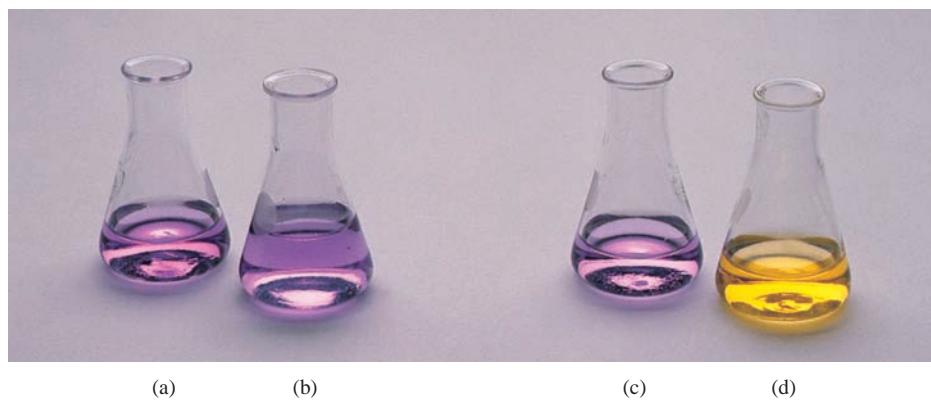


EACH 100 mL CONTAINS DOBUTAMINE HYDROCHLORIDE USP EQUIVALENT TO 200 MG DOBUTAMINE SODIUM BISULFITE ADDED AS A STABILIZER. pH ADJUSTED WITH SODIUM HYDROXIDE AND/OR HYDROCHLORIC ACID. pH 3.5 (2.5 TO 5.5). OSMOLALITY 266 mOSMOLES (CALC.). STERILE. NONPYROGENIC. SINGLE DOSE CONTAINER. DRUG ADDITIVES SHOULD NOT BE MADE TO THIS SOLUTION. DOSAGE: INTRAVENOUSLY AS DIRECTED BY A PHYSICIAN. SEE DIRECTIONS. CAUTIONS. MUST NOT BE USED IN

Fluids for intravenous injection must include buffer systems to maintain the proper blood pH.



**Animation:**  
Buffer solutions  
ARIS, Animations

**Figure 17.1**

The acid-base indicator bromophenol blue (added to all solutions shown) is used to illustrate buffer action. The indicator's color is blue-purple above pH 4.6 and yellow below pH 3.0.

(a) A buffer solution made up of 50 mL of 0.1 M  $\text{CH}_3\text{COOH}$  and 50 mL of 0.1 M  $\text{CH}_3\text{COONa}$ . The solution has a pH of 4.7 and turns the indicator blue-purple. (b) After the addition of 40 mL of 0.1 M HCl solution to the solution in (a), the color remains blue-purple. (c) A 100-mL  $\text{CH}_3\text{COOH}$  solution whose pH is 4.7. (d) After the addition of 6 drops (about 0.3 mL) of 0.1 M HCl solution, the color turns yellow. Without buffer action, the pH of the solution decreases rapidly to less than 3.0 upon the addition of 0.1 M HCl.

The *buffering capacity*, that is, the effectiveness of the buffer solution, depends on the amounts of acid and conjugate base from which the buffer is made. The larger the amount, the greater the buffering capacity.

In general, a buffer system can be represented as salt/acid or conjugate base/acid. Thus, the sodium acetate–acetic acid buffer system can be written as  $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$  or  $\text{CH}_3\text{COO}^-/\text{CH}_3\text{COOH}$ . Figure 17.1 shows this buffer system in action.

### Example 17.1

Which of the following solutions can be classified as buffer systems? (a)  $\text{KH}_2\text{PO}_4/\text{H}_3\text{PO}_4$ , (b)  $\text{NaClO}_4/\text{HClO}_4$ , (c)  $\text{C}_5\text{H}_5\text{N}/\text{C}_5\text{H}_5\text{NHCl}$  ( $\text{C}_5\text{H}_5\text{N}$  is pyridine; its  $K_b$  is given in Table 16.5). Explain your answer.

**Strategy** What constitutes a buffer system? Which of the preceding solutions contains a weak acid and its salt (containing the weak conjugate base)? Which of the preceding solutions contains a weak base and its salt (containing the weak conjugate acid)? Why is the conjugate base of a strong acid not able to neutralize an added acid?

**Solution** The criteria for a buffer system is that we must have a weak acid and its salt (containing the weak conjugate base) or a weak base and its salt (containing the weak conjugate acid).

- $\text{H}_3\text{PO}_4$  is a weak acid, and its conjugate base,  $\text{H}_2\text{PO}_4^-$ , is a weak base (see Table 16.4). Therefore, this is a buffer system.
- Because  $\text{HClO}_4$  is a strong acid, its conjugate base,  $\text{ClO}_4^-$ , is an extremely weak base. This means that the  $\text{ClO}_4^-$  ion will not combine with a  $\text{H}^+$  ion in solution to form  $\text{HClO}_4$ . Thus, the system cannot act as a buffer system.
- As Table 16.5 shows,  $\text{C}_5\text{H}_5\text{N}$  is a weak base and its conjugate acid,  $\text{C}_5\text{H}_5\text{NH}^+$  (the cation of the salt  $\text{C}_5\text{H}_5\text{NHCl}$ ), is a weak acid. Therefore, this is a buffer system.

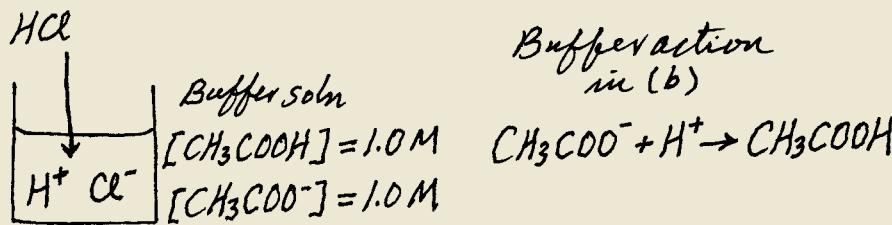
Similar problems: 17.5, 17.6.

**Practice Exercise** Which of the following are buffer systems? (a)  $\text{KF}/\text{HF}$ , (b)  $\text{KBr}/\text{HBr}$ , (c)  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ .

### Example 17.2

(a) Calculate the pH of a buffer system containing 1.0 M CH<sub>3</sub>COOH and 1.0 M CH<sub>3</sub>COONa. (b) What is the pH of the buffer system after the addition of 0.10 mole of gaseous HCl to 1.0 L of the solution? Assume that the volume of the solution does not change when the HCl is added.

**Strategy** (a) The pH of the buffer solution before the addition of HCl can be calculated from the ionization of CH<sub>3</sub>COOH. Note that because both the acid and the sodium salt of the acid are present, the initial concentrations of CH<sub>3</sub>COOH and CH<sub>3</sub>COO<sup>-</sup> (from CH<sub>3</sub>COONa) are both 1.0 M. The  $K_a$  of CH<sub>3</sub>COOH is  $1.8 \times 10^{-5}$  (see Table 16.3). (b) It is helpful to make a sketch of the changes that occur in this case.



**Solution** (a) We summarize the concentrations of the species at equilibrium as follows:

|  |  |      |           |
|--|--|------|-----------|
|  | $\text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)$ |      |           |
| Initial (M):   | 1.0  | 0    | 1.0       |
| Change (M):  | $-x$   | $+x$ | $+x$      |
| Equilibrium (M):   | $1.0 - x$  | $x$  | $1.0 + x$ |
| $K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$ |  |      |           |
| $1.8 \times 10^{-5} = \frac{(x)(1.0 + x)}{(1.0 - x)}$                          |  |      |           |

Assuming  $1.0 + x \approx 1.0$  and  $1.0 - x \approx 1.0$ , we obtain

$$1.8 \times 10^{-5} = \frac{(x)(1.0 + x)}{(1.0 - x)} \approx \frac{x(1.0)}{1.0}$$

or

$$x = [\text{H}^+] = 1.8 \times 10^{-5} \text{ M}$$

Thus,

$$\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$$

Recall that the presence of CH<sub>3</sub>COOH suppresses the hydrolysis of CH<sub>3</sub>COO<sup>-</sup> and the presence of CH<sub>3</sub>COO<sup>-</sup> suppresses the ionization of CH<sub>3</sub>COOH.

(b) When HCl is added to the solution, the initial changes are

|                |   |         |         |
|----------------|---|---------|---------|
|                | $\text{HCl}(aq) \longrightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$ |         |         |
| Initial (mol): | 0.10  | 0       | 0       |
| Change (mol):  | $-0.10$   | $+0.10$ | $+0.10$ |
| Final (mol):   | 0   | 0.10    | 0.10    |

The Cl<sup>-</sup> ion is a spectator ion in solution because it is the conjugate base of a strong acid.

The H<sup>+</sup> ions provided by the strong acid HCl react completely with the conjugate base of the buffer, which is CH<sub>3</sub>COO<sup>-</sup>. At this point it is more convenient to work with moles rather than molarity. The reason is that in some cases the volume of the solution may change when a substance is added. A change

(Continued)

in volume will change the molarity, but not the number of moles. The neutralization reaction is summarized next:

|                |                               |  |
|----------------|-------------------------------|--|
|                | $\text{CH}_3\text{COO}^-(aq)$ | $+\text{H}^+(aq) \longrightarrow \text{CH}_3\text{COOH}(aq)$ |
| Initial (mol): | 1.0                           | 0.10   |
| Change (mol):  | -0.10                         | -0.10  |
| Final (mol):   | 0.90                          | 0  |
|                |                               | 1.1  |

Finally, to calculate the pH of the buffer after neutralization of the acid, we convert back to molarity by dividing moles by 1.0 L of solution.

|                  |  |    |
|------------------|--|----|
|                  | $\text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)$ |    |
| Initial (M):     | 1.1  | 0  |
| Change (M):      | -x   | +x |
| Equilibrium (M): | $1.1 - x$  | x  |
|                  | $K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$               |    |
|                  | $1.8 \times 10^{-5} = \frac{(x)(0.90 + x)}{1.1 - x}$   |    |

Assuming  $0.90 + x \approx 0.90$  and  $1.1 - x \approx 1.1$ , we obtain

$$1.8 \times 10^{-5} = \frac{(x)(0.90 + x)}{1.1 - x} \approx \frac{x(0.90)}{1.1}$$

or

$$x = [\text{H}^+] = 2.2 \times 10^{-5} M$$

**Similar problem: 17.14**

**Practice Exercise** Calculate the pH of the  $0.30\text{ M}$   $\text{NH}_3/0.36\text{ M}$   $\text{NH}_4\text{Cl}$  buffer system. What is the pH after the addition of 20.0 mL of  $0.050\text{ M}$   $\text{NaOH}$  to 80.0 mL of the buffer solution?

In the buffer solution examined in Example 17.2, there is a decrease in pH (the solution becomes more acidic) as a result of added HCl. We can also compare the changes in  $\text{H}^+$  ion concentration as follows

Before addition of HCl:  $[\text{H}^+] = 1.8 \times 10^{-5} M$

After addition of HCl:  $[\text{H}^+] = 2.2 \times 10^{-5} M$

Thus, the  $\text{H}^+$  ion concentration increases by a factor of

$$\frac{2.2 \times 10^{-5} M}{1.8 \times 10^{-5} M} = 1.2$$

To appreciate the effectiveness of the  $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$  buffer, let us find out what would happen if 0.10 mol HCl were added to 1 L of water, and compare the increase in  $\text{H}^+$  ion concentration.

Before addition of HCl:  $[\text{H}^+] = 1.0 \times 10^{-7} M$

After addition of HCl:  $[\text{H}^+] = 0.10 M$

As a result of the addition of HCl, the  $\text{H}^+$  ion concentration increases by a factor of

$$\frac{0.10 M}{1.0 \times 10^{-7} M} = 1.0 \times 10^6$$

amounting to a millionfold increase! This comparison shows that a properly chosen buffer solution can maintain a fairly constant  $\text{H}^+$  ion concentration, or pH (Figure 17.2).

## Preparing a Buffer Solution with a Specific pH

Now suppose we want to prepare a buffer solution with a specific pH. How do we go about it? Referring to the acetic acid–sodium acetate buffer system, we can write the equilibrium constant as

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

Note that this expression holds whether we have only acetic acid or a mixture of acetic acid and sodium acetate in solution. Rearranging the equation gives

$$[\text{H}^+] = \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

Taking the negative logarithm of both sides, we obtain

$$-\log [\text{H}^+] = -\log K_a - \log \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

or

$$-\log [\text{H}^+] = -\log K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

So

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad (17.1)$$

in which

$$\text{p}K_a = -\log K_a \quad (17.2)$$

Equation (17.1) is called the *Henderson-Hasselbalch equation*. In a more general form, it can be expressed as

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]} \quad (17.3)$$

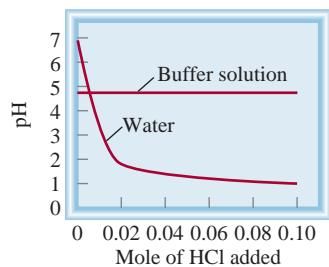
If the molar concentrations of the acid and its conjugate base are approximately equal, that is,  $[\text{acid}] \approx [\text{conjugate base}]$ , then

$$\log \frac{[\text{conjugate base}]}{[\text{acid}]} \approx 0$$

or

$$\text{pH} \approx \text{p}K_a$$

Thus, to prepare a buffer solution, we choose a weak acid whose  $\text{p}K_a$  is close to the desired pH. This choice not only gives the correct pH value of the buffer system, but also ensures that we have *comparable* amounts of the acid and its conjugate base present; both are prerequisites for the buffer system to function effectively.



**Figure 17.2**

A comparison of the change in pH when 0.10 mol HCl is added to pure water and to an acetate buffer solution, as described in Example 17.2.

$\text{p}K_a$  is related to  $K_a$  as pH is related to  $[\text{H}^+]$ . Remember that the stronger the acid (that is, the larger the  $K_a$ ), the smaller the  $\text{p}K_a$ .

Keep in mind that  $\text{p}K_a$  is a constant, but the ratio of the two concentration terms in Equation (17.3) depends on a particular solution.

### Example 17.3

Describe how you would prepare a “phosphate buffer” with a pH of about 7.40.

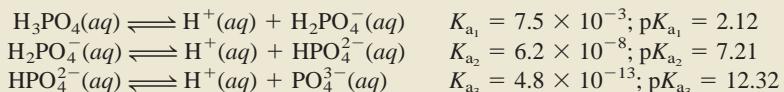
**Strategy** For a buffer to function effectively, the concentrations of the acid component must be roughly equal to the conjugate base component. According to Equation (17.3), when the desired pH is close to the  $pK_a$  of the acid, that is, when  $\text{pH} \approx pK_a$ ,

$$\log \frac{[\text{conjugate base}]}{[\text{acid}]} \approx 0$$

or

$$\frac{[\text{conjugate base}]}{[\text{acid}]} \approx 1$$

**Solution** Because phosphoric acid is a triprotic acid, we write the three stages of ionization as follows. The  $K_a$  values are obtained from Table 16.4 and the  $pK_a$  values are found by applying Equation (17.2).



The most suitable of the three buffer systems is  $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$ , because the  $pK_a$  of the acid  $\text{H}_2\text{PO}_4^-$  is closest to the desired pH. From the Henderson-Hasselbalch equation we write

$$\begin{aligned} \text{pH} &= pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]} \\ 7.40 &= 7.21 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \\ \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} &= 0.19 \end{aligned}$$

Taking the antilog, we obtain

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 10^{0.19} = 1.5$$

Thus, one way to prepare a phosphate buffer with a pH of 7.40 is to dissolve disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) and sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) in a mole ratio of 1.5:1.0 in water. For example, we could dissolve 1.5 moles of  $\text{Na}_2\text{HPO}_4$  and 1.0 mole of  $\text{NaH}_2\text{PO}_4$  in enough water to make up a 1-L solution.

**Practice Exercise** How would you prepare a liter of “carbonate buffer” at a pH of 10.10? You are provided with carbonic acid ( $\text{H}_2\text{CO}_3$ ), sodium hydrogen carbonate ( $\text{NaHCO}_3$ ), and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). See Table 16.4 for  $K_a$  values.

## 17.3 A Closer Look at Acid-Base Titrations



**Animation:**  
Acid-Base Titrations  
ARIS, Animations

Having discussed buffer solutions, we can now look in more detail at the quantitative aspects of acid-base titrations (see Section 4.6). We will consider three types of reactions: (1) titrations involving a strong acid and a strong base, (2) titrations involving a weak acid and a strong base, and (3) titrations involving a strong acid and a weak base. Titrations



**Figure 17.3**  
A pH meter is used to monitor an acid-base titration.

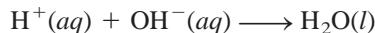
involving a weak acid and a weak base are complicated by the hydrolysis of both the cation and the anion of the salt formed. These titrations will not be dealt with here. Figure 17.3 shows the arrangement for monitoring the pH during the course of a titration.

## Strong Acid–Strong Base Titrations

The reaction between a strong acid (say, HCl) and a strong base (say, NaOH) can be represented by



or in terms of the net ionic equation



Consider the addition of a 0.100  $M$  NaOH solution (from a buret) to an Erlenmeyer flask containing 25.0 mL of 0.100  $M$  HCl. For convenience, we will use only three significant figures for volume and concentration and two significant figures for pH. Figure 17.4 shows the pH profile of the titration (also known as the titration curve). Before the addition of NaOH, the pH of the acid is given by  $-\log(0.100)$ , or 1.00. When NaOH is added, the pH of the solution increases slowly at first. Near the equivalence point the pH begins to rise steeply, and at the equivalence point (that is, the point at which equimolar amounts of acid and base have reacted) the curve rises almost vertically. In a strong acid–strong base titration both the hydrogen ion and hydroxide ion concentrations are very small at the equivalence point (approximately  $1 \times 10^{-7} M$ ); consequently, the addition of a single drop of the base can cause a large increase in  $[\text{OH}^-]$  and in the pH of the solution. Beyond the equivalence point, the pH again increases slowly with the addition of NaOH.

It is possible to calculate the pH of the solution at every stage of titration. Here are three sample calculations:

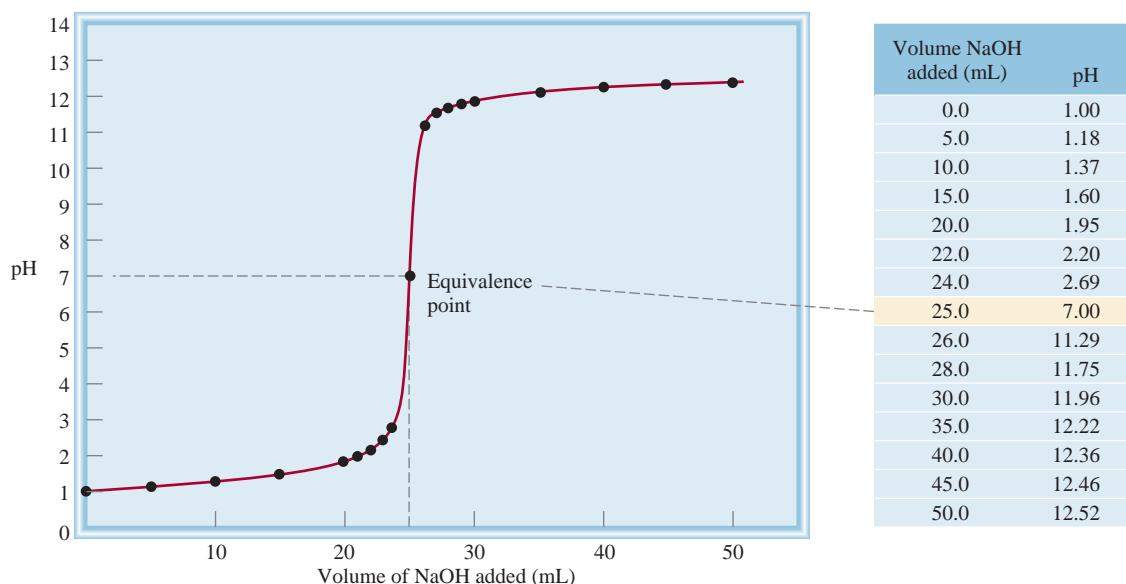
1. After the addition of 10.0 mL of 0.100  $M$  NaOH to 25.0 mL of 0.100  $M$  HCl.

The total volume of the solution is 35.0 mL. The number of moles of NaOH in 10.0 mL is

$$10.0 \text{ mL} \times \frac{0.100 \text{ mol NaOH}}{1 \text{ L NaOH}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 1.00 \times 10^{-3} \text{ mol}$$



**Interactivity:**  
Neutralization Reaction I and II  
ARIS, Interactives

**Figure 17.4**

pH profile of a strong acid-strong base titration. A 0.100 M NaOH solution is added from a buret to 25.0 mL of a 0.100 M HCl solution in an Erlenmeyer flask (see Figure 4.21). This curve is sometimes referred to as a titration curve.

The number of moles of HCl originally present in 25.0 mL of solution is

$$25.0 \text{ mL} \times \frac{0.100 \text{ mol HCl}}{1 \text{ L HCl}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 2.50 \times 10^{-3} \text{ mol}$$

Keep in mind that 1 mol NaOH  $\approx$  1 mol HCl.

Thus, the amount of HCl left after partial neutralization is  $(2.50 \times 10^{-3}) - (1.00 \times 10^{-3})$ , or  $1.50 \times 10^{-3}$  mol. Next, the concentration of  $\text{H}^+$  ions in 35.0 mL of solution is found as follows:

$$\frac{1.50 \times 10^{-3} \text{ mol HCl}}{35.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.0429 \text{ mol HCl/L}$$

$$= 0.0429 \text{ M HCl}$$

Thus,  $[\text{H}^+] = 0.0429 \text{ M}$ , and the pH of the solution is

$$\text{pH} = -\log 0.0429 = 1.37$$

Neither  $\text{Na}^+$  nor  $\text{Cl}^-$  undergoes hydrolysis.

- After the addition of 25.0 mL of 0.100 M NaOH to 25.0 mL of 0.100 M HCl. This is a simple calculation, because it involves a complete neutralization reaction and the salt (NaCl) does not undergo hydrolysis. At the equivalence point,  $[\text{H}^+] = [\text{OH}^-] = 1.00 \times 10^{-7} \text{ M}$  and the pH of the solution is 7.00.
- After the addition of 35.0 mL of 0.100 M NaOH to 25.0 mL of 0.100 M HCl. The total volume of the solution is now 60.0 mL. The number of moles of NaOH added is

$$35.0 \text{ mL} \times \frac{0.100 \text{ mol NaOH}}{1 \text{ L NaOH}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 3.50 \times 10^{-3} \text{ mol}$$

The number of moles of HCl in 25.0 mL solution is  $2.50 \times 10^{-3}$  mol. After complete neutralization of HCl, the number of moles of NaOH left is

$(3.50 \times 10^{-3}) - (2.50 \times 10^{-3})$ , or  $1.00 \times 10^{-3}$  mol. The concentration of NaOH in 60.0 mL of solution is

$$\frac{1.00 \times 10^{-3} \text{ mol NaOH}}{60.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.0167 \text{ mol NaOH/L}$$

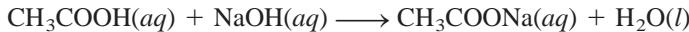
$$= 0.0167 M \text{ NaOH}$$

Thus,  $[\text{OH}^-] = 0.0167 M$  and  $\text{pOH} = -\log 0.0167 = 1.78$ . Hence, the pH of the solution is

$$\begin{aligned}\text{pH} &= 14.00 - \text{pOH} \\ &= 14.00 - 1.78 \\ &= 12.22\end{aligned}$$

## Weak Acid–Strong Base Titrations

Consider the neutralization reaction between acetic acid (a weak acid) and sodium hydroxide (a strong base):



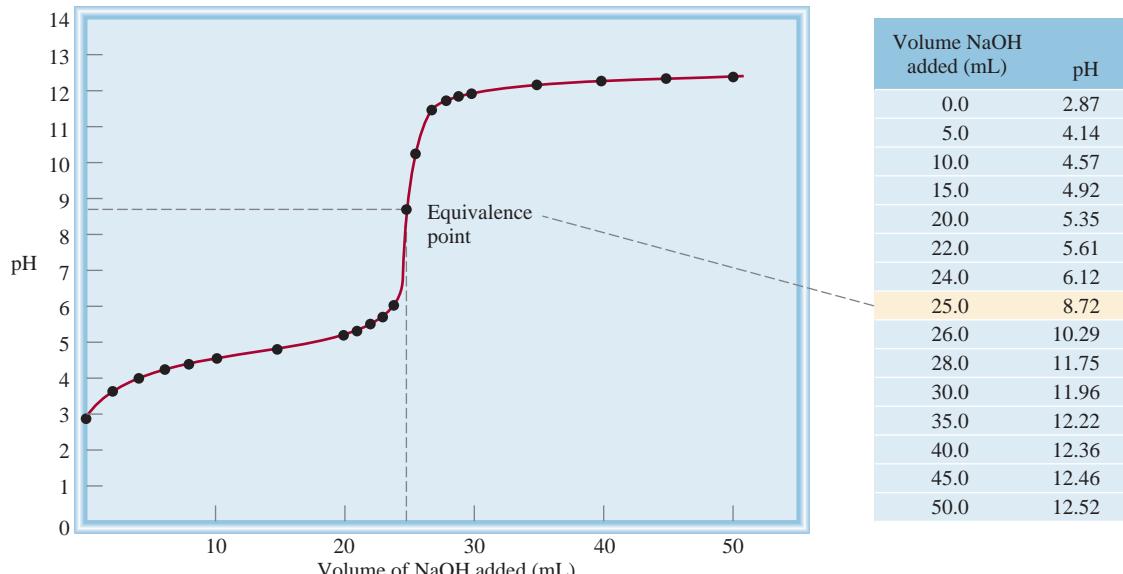
This equation can be simplified to



The acetate ion undergoes hydrolysis as follows:



Therefore, at the equivalence point, when we only have sodium acetate present, the pH will be *greater than* 7 as a result of the excess  $\text{OH}^-$  ions formed (Figure 17.5). Note that this situation is analogous to the hydrolysis of sodium acetate ( $\text{CH}_3\text{COONa}$ ) (see p. 558).



**Figure 17.5**

pH profile of a weak acid–strong base titration. A 0.100 M NaOH solution is added from a buret to 25.0 mL of a 0.100 M  $\text{CH}_3\text{COOH}$  solution in an Erlenmeyer flask. Due to the hydrolysis of the salt formed, the pH at the equivalence point is greater than 7.

### Example 17.4

Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid by sodium hydroxide after the addition to the acid solution of (a) 10.0 mL of 0.100 M NaOH, (b) 25.0 mL of 0.100 M NaOH, (c) 35.0 mL of 0.100 M NaOH.

**Strategy** The reaction between  $\text{CH}_3\text{COOH}$  and NaOH is



We see that 1 mol  $\text{CH}_3\text{COOH} \approx$  1 mol NaOH. Therefore, at every stage of the titration we can calculate the number of moles of base reacting with the acid, and the pH of the solution is determined by the excess acid or base left over. At the equivalence point, however, the neutralization is complete and the pH of the solution will depend on the extent of the hydrolysis of the salt formed, which is  $\text{CH}_3\text{COONa}$ .

**Solution** (a) The number of moles of NaOH in 10.0 mL is

$$10.0 \text{ mL} \times \frac{0.100 \text{ mol NaOH}}{1 \text{ L NaOH soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 1.00 \times 10^{-3} \text{ mol}$$

The number of moles of  $\text{CH}_3\text{COOH}$  originally present in 25.0 mL of solution is

$$25.0 \text{ mL} \times \frac{0.100 \text{ mol CH}_3\text{COOH}}{1 \text{ L CH}_3\text{COOH soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 2.50 \times 10^{-3} \text{ mol}$$

We work with moles at this point because when two solutions are mixed, the solution volume increases. As the volume increases, molarity will change but the number of moles will remain the same. The changes in number of moles are summarized next:

|                | $\text{CH}_3\text{COOH}(aq) + \text{NaOH}(aq) \longrightarrow \text{CH}_3\text{COONa}(aq) + \text{H}_2\text{O}(l)$ |                        |                        |
|----------------|--|------------------------|------------------------|
| Initial (mol): | $2.50 \times 10^{-3}$  | $1.00 \times 10^{-3}$  | 0                      |
| Change (mol):  | $-1.00 \times 10^{-3}$   | $-1.00 \times 10^{-3}$ | $+1.00 \times 10^{-3}$ |
| Final (mol):   | $1.50 \times 10^{-3}$  | 0                      | $1.00 \times 10^{-3}$  |

At this stage we have a buffer system made up of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  (from the salt,  $\text{CH}_3\text{COONa}$ ). To calculate the pH of the solution, we write

$$\begin{aligned} K_a &= \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \\ [\text{H}^+] &= \frac{[\text{CH}_3\text{COOH}]K_a}{[\text{CH}_3\text{COO}^-]} \\ &= \frac{(1.50 \times 10^{-3})(1.8 \times 10^{-5})}{1.00 \times 10^{-3}} = 2.7 \times 10^{-5} \text{ M} \end{aligned}$$

Therefore,

$$\text{pH} = -\log(2.7 \times 10^{-5}) = 4.57$$

Because the volume of the solution is the same for  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$ , the ratio of the number of moles present is equal to the ratio of their molar concentrations.

- (b) These quantities (that is, 25.0 mL of 0.100 M NaOH reacting with 25.0 mL of 0.100 M  $\text{CH}_3\text{COOH}$ ) correspond to the equivalence point. The number of moles of NaOH in 25.0 mL of the solution is

$$25.0 \text{ mL} \times \frac{0.100 \text{ mol NaOH}}{1 \text{ L NaOH soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 2.50 \times 10^{-3} \text{ mol}$$

(Continued)

The changes in number of moles are summarized next:

|                |                              |                        |                   |                               |                          |
|----------------|------------------------------|------------------------|-------------------|-------------------------------|--------------------------|
|                | $\text{CH}_3\text{COOH}(aq)$ | $\text{NaOH}(aq)$      | $\longrightarrow$ | $\text{CH}_3\text{COONa}(aq)$ | $+\text{H}_2\text{O}(l)$ |
| Initial (mol): | $2.50 \times 10^{-3}$        | $2.50 \times 10^{-3}$  |                   | 0                             |                          |
| Change (mol):  | $-2.50 \times 10^{-3}$       | $-2.50 \times 10^{-3}$ |                   | $+2.50 \times 10^{-3}$        |                          |
| Final (mol):   | 0                            | 0                      |                   | $2.50 \times 10^{-3}$         |                          |

At the equivalence point, the concentrations of both the acid and the base are zero. The total volume is  $(25.0 + 25.0)$  mL or 50.0 mL, so the concentration of the salt is

$$[\text{CH}_3\text{COONa}] = \frac{2.50 \times 10^{-3} \text{ mol}}{50.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \\ = 0.0500 \text{ mol/L} = 0.0500 \text{ M}$$

The next step is to calculate the pH of the solution that results from the hydrolysis of the  $\text{CH}_3\text{COO}^-$  ions. Following the procedure described in Example 16.13 and looking up the base ionization constant ( $K_b$ ) for  $\text{CH}_3\text{COO}^-$  in Table 16.3, we write

$$K_b = 5.6 \times 10^{-10} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{x^2}{0.0500 - x} \\ x = [\text{OH}^-] = 5.3 \times 10^{-6} \text{ M}, \text{pH} = 8.72$$

- (c) After the addition of 35.0 mL of NaOH, the solution is well past the equivalence point. The number of moles of NaOH originally present is

$$35.0 \text{ mL} \times \frac{0.100 \text{ mol NaOH}}{1 \text{ L NaOH soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 3.50 \times 10^{-3} \text{ mol}$$

The changes in number of moles are summarized next:

|                |                              |                        |                   |                               |                          |
|----------------|------------------------------|------------------------|-------------------|-------------------------------|--------------------------|
|                | $\text{CH}_3\text{COOH}(aq)$ | $\text{NaOH}(aq)$      | $\longrightarrow$ | $\text{CH}_3\text{COONa}(aq)$ | $+\text{H}_2\text{O}(l)$ |
| Initial (mol): | $2.50 \times 10^{-3}$        | $3.50 \times 10^{-3}$  |                   | 0                             |                          |
| Change (mol):  | $-2.50 \times 10^{-3}$       | $-2.50 \times 10^{-3}$ |                   | $+2.50 \times 10^{-3}$        |                          |
| Final (mol):   | 0                            | $1.00 \times 10^{-3}$  |                   | $2.50 \times 10^{-3}$         |                          |

At this stage we have two species in solution that are responsible for making the solution basic:  $\text{OH}^-$  and  $\text{CH}_3\text{COO}^-$  (from  $\text{CH}_3\text{COONa}$ ). However, because  $\text{OH}^-$  is a much stronger base than  $\text{CH}_3\text{COO}^-$ , we can safely neglect the hydrolysis of the  $\text{CH}_3\text{COO}^-$  ions and calculate the pH of the solution using only the concentration of the  $\text{OH}^-$  ions. The total volume of the combined solutions is  $(25.0 + 35.0)$  mL or 60.0 mL, so we calculate  $\text{OH}^-$  concentration as follows:

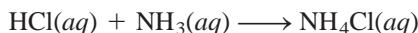
$$[\text{OH}^-] = \frac{1.00 \times 10^{-3} \text{ mol}}{60.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \\ = 0.0167 \text{ mol/L} = 0.0167 \text{ M} \\ \text{pOH} = -\log [\text{OH}^-] = -\log 0.0167 = 1.78 \\ \text{pH} = 14.00 - 1.78 = 12.22$$

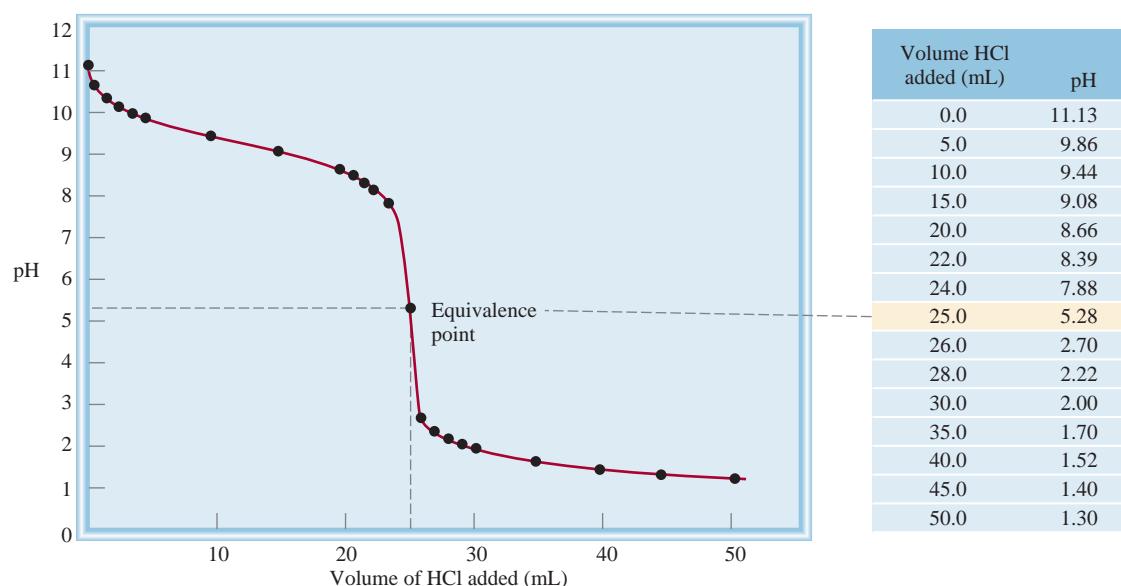
Similar problem: 17.19(b).

**Practice Exercise** Exactly 100 mL of 0.10 M nitrous acid ( $\text{HNO}_2$ ) are titrated with a 0.10 M NaOH solution. Calculate the pH for (a) the initial solution, (b) the point at which 80 mL of the base has been added, (c) the equivalence point, (d) the point at which 105 mL of the base has been added.

## Strong Acid–Weak Base Titrations

Consider the titration of HCl, a strong acid, with  $\text{NH}_3$ , a weak base:



**Figure 17.6**

pH profiles of a strong acid–weak base titration. A 0.100 M HCl solution is added from a buret to 25.0 mL of a 0.100 M NH<sub>3</sub> solution in an Erlenmeyer flask. As a result of salt hydrolysis, the pH at the equivalence point is lower than 7.

or simply



The pH at the equivalence point is *less than* 7 due to the hydrolysis of the NH<sub>4</sub><sup>+</sup> ion:



or simply



Because of the volatility of an aqueous ammonia solution, it is more convenient to add hydrochloric acid from a buret to the ammonia solution. Figure 17.6 shows the titration curve for this experiment.

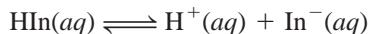
## 17.4 Acid-Base Indicators

The equivalence point, as we have seen, is the point at which the number of moles of OH<sup>-</sup> ions added to a solution is equal to the number of moles of H<sup>+</sup> ions originally present. To determine the equivalence point in a titration, then, we must know exactly how much volume of a base to add from a buret to an acid in a flask. One way to achieve this goal is to add a few drops of an acid-base indicator to the acid solution at the start of the titration. You will recall from Chapter 4 that an indicator has distinctly different colors in its nonionized and ionized forms. These two forms are related to the pH of the solution in which the indicator is dissolved. The ***end point*** of a titration occurs when the indicator changes color. However, not all indicators change color at the same pH, so the choice of

An indicator is usually a weak organic acid or organic base. Only a small amount (a drop or two) should be used in a titration experiment.

indicator for a particular titration depends on the nature of the acid and base used in the titration (that is, whether they are strong or weak). By choosing the proper indicator for a titration, we can use the end point to determine the equivalence point, as we will see next.

Let us consider a weak monoprotic acid that we will call HIn. To be an effective indicator, HIn and its conjugate base,  $\text{In}^-$ , must have distinctly different colors. In solution, the acid ionizes to a small extent:



If the indicator is in a sufficiently acidic medium, the equilibrium, according to Le Châtelier's principle, shifts to the left and the predominant color of the indicator is that of the nonionized form (HIn). On the other hand, in a basic medium the equilibrium shifts to the right and the color of the solution will be due mainly to that of the conjugate base ( $\text{In}^-$ ). Roughly speaking, we can use the following concentration ratios to predict the perceived color of the indicator:

$$\frac{[\text{HIn}]}{[\text{In}^-]} \geq 10 \quad \text{color of acid (HIn) predominates}$$

$$\frac{[\text{HIn}]}{[\text{In}^-]} \leq 0.1 \quad \text{color of conjugate base (In}^-)\text{ predominates}$$

If  $[\text{HIn}] \approx [\text{In}^-]$ , then the indicator color is a combination of the colors of HIn and  $\text{In}^-$ .

The end point of an indicator does not occur at a specific pH; rather, there is a range of pH values within which the end point will occur. In practice, we choose an indicator whose end point range lies on the steep part of the titration curve. Because the equivalence point also lies on the steep part of the curve, this choice ensures that the pH at the equivalence point will fall within the range over which the indicator changes color. In Section 4.6 we mentioned that phenolphthalein is a suitable indicator for the titration of NaOH and HCl. Phenolphthalein is colorless in acidic and neutral solutions, but reddish pink in basic solutions. Measurements show that at  $\text{pH} < 8.3$  the indicator is colorless but that it begins to turn reddish pink when the pH exceeds 8.3. As shown in Figure 17.4, the steepness of the pH curve near the equivalence point means that the addition of a very small quantity of NaOH (say, 0.05 mL, which is about the volume of a drop from the buret) brings about a large rise in the pH of the solution. What is important, however, is the fact that the steep portion of the pH profile includes the range over which phenolphthalein changes from colorless to reddish pink. Whenever such a correspondence occurs, the indicator can be used to locate the equivalence point of the titration (Figure 17.7).

Many acid-base indicators are plant pigments. For example, by boiling chopped red cabbage in water we can extract pigments that exhibit many different colors at various pHs (Figure 17.8). Table 17.1 lists a number of indicators commonly used in acid-base titrations. The choice of a particular indicator depends on the strength of the acid and base to be titrated.

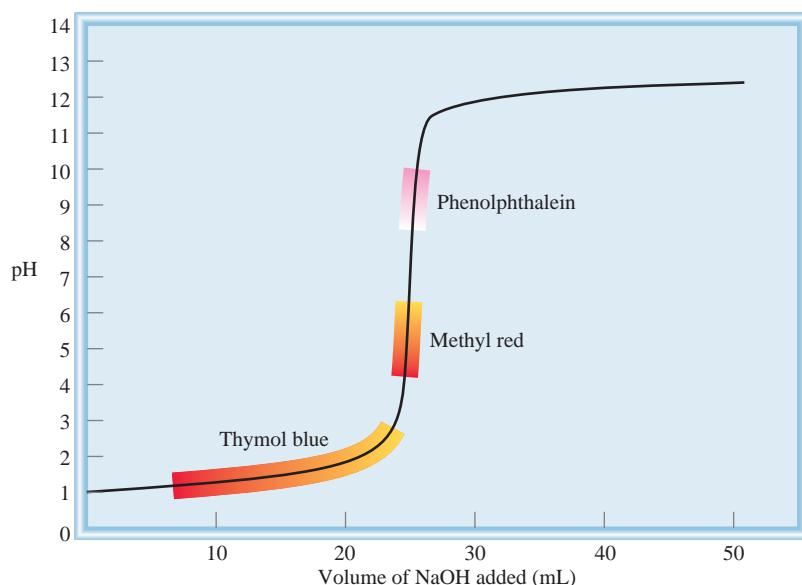
### Example 17.5

Which indicator or indicators listed in Table 17.1 would you use for the acid-base titrations shown in (a) Figure 17.4, (b) Figure 17.5, and (c) Figure 17.6.

(Continued)

**Figure 17.7**

The titration curve of a strong acid with a strong base. Because the regions over which the indicators methyl red and phenolphthalein change color along the steep portion of the curve, they can be used to monitor the equivalence point of the titration. Thymol blue, on the other hand, cannot be used for the same purpose (see Table 17.1).



**Strategy** The choice of an indicator for a particular titration is based on the fact that its pH range for color change must overlap the steep portion of the titration curve. Otherwise we cannot use the color change to locate the equivalence point.

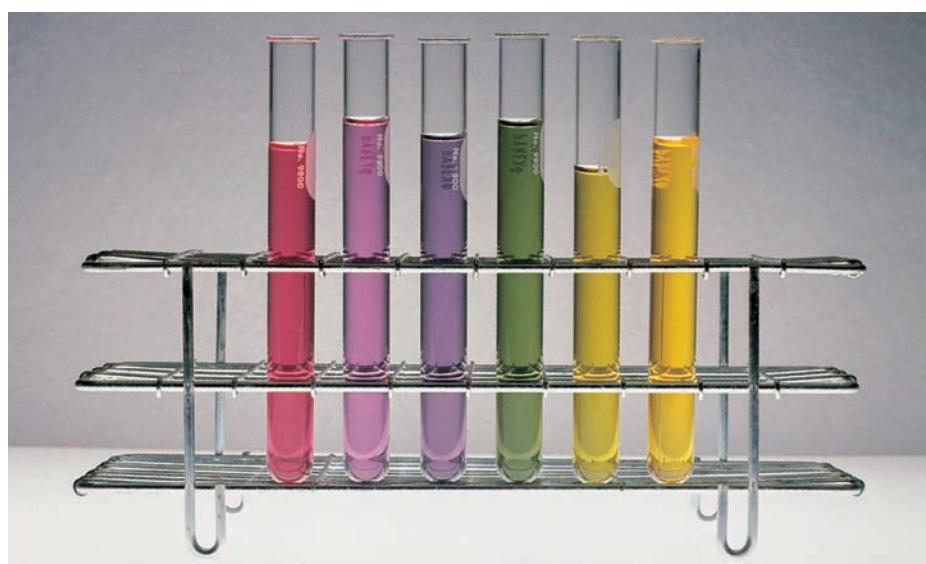
- Solution**
- Near the equivalence point, the pH of the solution changes abruptly from 4 to 10. Therefore, all the indicators except thymol blue, bromophenol blue, and methyl orange are suitable for use in the titration.
  - Here the steep portion covers the pH range between 7 and 10; therefore, the suitable indicators are cresol red and phenolphthalein.
  - Here the steep portion of the pH curve covers the pH range between 3 and 7; therefore, the suitable indicators are bromophenol blue, methyl orange, methyl red, and chlorophenol blue.

Similar problem: 17.25.

(Continued)

**Figure 17.8**

Solutions containing extracts of red cabbage (obtained by boiling the cabbage in water) produce different colors when treated with an acid and a base. The pH of the solutions increases from left to right.



**TABLE 17.1** Some Common Acid-Base Indicators

| Indicator         | Color     |               | pH Range* |
|-------------------|-----------|---------------|-----------|
|                   | In Acid   | In Base       |           |
| Thymol blue       | Red       | Yellow        | 1.2–2.8   |
| Bromophenol blue  | Yellow    | Bluish purple | 3.0–4.6   |
| Methyl orange     | Orange    | Yellow        | 3.1–4.4   |
| Methyl red        | Red       | Yellow        | 4.2–6.3   |
| Chlorophenol blue | Yellow    | Red           | 4.8–6.4   |
| Bromothymol blue  | Yellow    | Blue          | 6.0–7.6   |
| Cresol red        | Yellow    | Red           | 7.2–8.8   |
| Phenolphthalein   | Colorless | Reddish pink  | 8.3–10.0  |

\*The pH range is defined as the range over which the indicator changes from the acid color to the base color.

**Practice Exercise** Referring to Table 17.1, specify which indicator or indicators you would use for the following titrations: (a) HBr versus  $\text{CH}_3\text{NH}_2$ , (b)  $\text{HNO}_3$  versus NaOH, (c)  $\text{HNO}_2$  versus KOH.

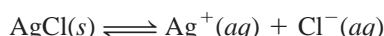
## 17.5 Solubility Equilibria

Precipitation reactions are important in industry, medicine, and everyday life. For example, the preparation of many essential industrial chemicals such as sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) makes use of precipitation reactions. The dissolving of tooth enamel, which is mainly made of hydroxyapatite [ $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ], in an acidic medium leads to tooth decay. Barium sulfate ( $\text{BaSO}_4$ ), an insoluble compound that is opaque to X rays, is used to diagnose ailments of the digestive tract. Stalactites and stalagmites, which consist of calcium carbonate ( $\text{CaCO}_3$ ), are produced by a precipitation reaction, and so are many foods, such as fudge.

The general rules for predicting the solubility of ionic compounds in water were introduced in Section 4.2. Although useful, these solubility rules do not enable us to make quantitative predictions about how much of a given ionic compound will dissolve in water. To develop a quantitative approach, we start with what we already know about chemical equilibrium.

### Solubility Product

Consider a saturated solution of silver chloride that is in contact with solid silver chloride. The solubility equilibrium can be represented as

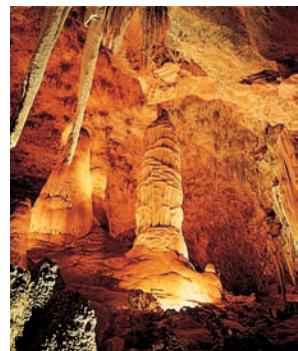


Because salts such as  $\text{AgCl}$  are treated as strong electrolytes, all the  $\text{AgCl}$  that dissolves in water is assumed to dissociate completely into  $\text{Ag}^+$  and  $\text{Cl}^-$  ions. We know from Chapter 15 that for heterogeneous reactions the concentration of the solid is a constant. Thus, we can write the equilibrium constant for the dissociation of  $\text{AgCl}$  as

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$



$\text{BaSO}_4$  imaging of the human large intestine.



Downward-growing stalactites and upward-growing stalagmites.

in which  $K_{sp}$  is called the solubility product constant or simply the solubility product. In general, the *solubility product* of a compound is *the product of the molar concentrations of the constituent ions, each raised to the power of its stoichiometric coefficient in the equilibrium equation.*

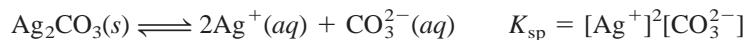
Because each  $\text{AgCl}$  unit contains only one  $\text{Ag}^+$  ion and one  $\text{Cl}^-$  ion, its solubility product expression is particularly simple to write. The following cases are more complex.

- $\text{MgF}_2$

We ignore both ion pair formation and salt hydrolysis (see p. 533).



- $\text{Ag}_2\text{CO}_3$



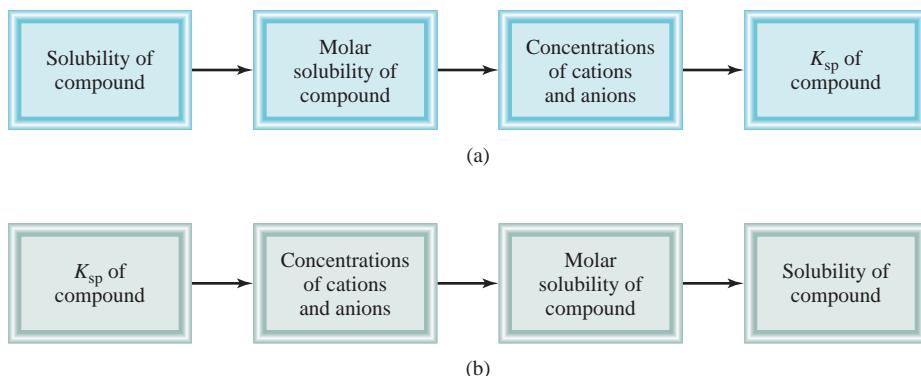
- $\text{Ca}_3(\text{PO}_4)_2$



Table 17.2 lists the  $K_{sp}$  values for a number of salts of low solubility. Soluble salts such as  $\text{NaCl}$  and  $\text{KNO}_3$ , which have very large  $K_{sp}$  values, are not listed in the table.

**TABLE 17.2** Solubility Products of Some Slightly Soluble Ionic Compounds at 25°C

| Compound   | $K_{sp}$              | Compound   | $K_{sp}$              |
|--|-----------------------|--|-----------------------|
| Aluminum hydroxide $[\text{Al}(\text{OH})_3]$      | $1.8 \times 10^{-33}$ | Lead(II) chromate ( $\text{PbCrO}_4$ )           | $2.0 \times 10^{-14}$ |
| Barium carbonate ( $\text{BaCO}_3$ )               | $8.1 \times 10^{-9}$  | Lead(II) fluoride ( $\text{PbF}_2$ )             | $4.1 \times 10^{-8}$  |
| Barium fluoride ( $\text{BaF}_2$ )                 | $1.7 \times 10^{-6}$  | Lead(II) iodide ( $\text{PbI}_2$ )               | $1.4 \times 10^{-8}$  |
| Barium sulfate ( $\text{BaSO}_4$ )                 | $1.1 \times 10^{-10}$ | Lead(II) sulfide ( $\text{PbS}$ )                | $3.4 \times 10^{-28}$ |
| Bismuth sulfide ( $\text{Bi}_2\text{S}_3$ )        | $1.6 \times 10^{-72}$ | Magnesium carbonate ( $\text{MgCO}_3$ )          | $4.0 \times 10^{-5}$  |
| Cadmium sulfide ( $\text{CdS}$ )                   | $8.0 \times 10^{-28}$ | Magnesium hydroxide $[\text{Mg}(\text{OH})_2]$   | $1.2 \times 10^{-11}$ |
| Calcium carbonate ( $\text{CaCO}_3$ )              | $8.7 \times 10^{-9}$  | Manganese(II) sulfide ( $\text{MnS}$ )           | $3.0 \times 10^{-14}$ |
| Calcium fluoride ( $\text{CaF}_2$ )                | $4.0 \times 10^{-11}$ | Mercury(I) chloride ( $\text{Hg}_2\text{Cl}_2$ ) | $3.5 \times 10^{-18}$ |
| Calcium hydroxide $[\text{Ca}(\text{OH})_2]$       | $8.0 \times 10^{-6}$  | Mercury(II) sulfide ( $\text{HgS}$ )             | $4.0 \times 10^{-54}$ |
| Calcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$   | $1.2 \times 10^{-26}$ | Nickel(II) sulfide ( $\text{NiS}$ )              | $1.4 \times 10^{-24}$ |
| Chromium(III) hydroxide $[\text{Cr}(\text{OH})_3]$ | $3.0 \times 10^{-29}$ | Silver bromide ( $\text{AgBr}$ )                 | $7.7 \times 10^{-13}$ |
| Cobalt(II) sulfide ( $\text{CoS}$ )                | $4.0 \times 10^{-21}$ | Silver carbonate ( $\text{Ag}_2\text{CO}_3$ )    | $8.1 \times 10^{-12}$ |
| Copper(I) bromide ( $\text{CuBr}$ )                | $4.2 \times 10^{-8}$  | Silver chloride ( $\text{AgCl}$ )                | $1.6 \times 10^{-10}$ |
| Copper(I) iodide ( $\text{CuI}$ )                  | $5.1 \times 10^{-12}$ | Silver iodide ( $\text{AgI}$ )                   | $8.3 \times 10^{-17}$ |
| Copper(II) hydroxide $[\text{Cu}(\text{OH})_2]$    | $2.2 \times 10^{-20}$ | Silver sulfate ( $\text{Ag}_2\text{SO}_4$ )      | $1.4 \times 10^{-5}$  |
| Copper(II) sulfide ( $\text{CuS}$ )                | $6.0 \times 10^{-37}$ | Silver sulfide ( $\text{Ag}_2\text{S}$ )         | $6.0 \times 10^{-51}$ |
| Iron(II) hydroxide $[\text{Fe}(\text{OH})_2]$      | $1.6 \times 10^{-14}$ | Strontium carbonate ( $\text{SrCO}_3$ )          | $1.6 \times 10^{-9}$  |
| Iron(III) hydroxide $[\text{Fe}(\text{OH})_3]$     | $1.1 \times 10^{-36}$ | Strontium sulfate ( $\text{SrSO}_4$ )            | $3.8 \times 10^{-7}$  |
| Iron(II) sulfide ( $\text{FeS}$ )                  | $6.0 \times 10^{-19}$ | Tin(II) sulfide ( $\text{SnS}$ )                 | $1.0 \times 10^{-26}$ |
| Lead(II) carbonate ( $\text{PbCO}_3$ )             | $3.3 \times 10^{-14}$ | Zinc hydroxide $[\text{Zn}(\text{OH})_2]$        | $1.8 \times 10^{-14}$ |
| Lead(II) chloride ( $\text{PbCl}_2$ )              | $2.4 \times 10^{-4}$  | Zinc sulfide ( $\text{ZnS}$ )                    | $3.0 \times 10^{-23}$ |

**Figure 17.9**

Sequence of steps (a) for calculating  $K_{sp}$  from solubility data and (b) for calculating solubility from  $K_{sp}$  data.

For the dissolution of an ionic solid in aqueous solution, any one of the following conditions may exist: (1) The solution is unsaturated, (2) the solution is saturated, or (3) the solution is supersaturated. Following the procedure in Section 15.3, we use  $Q$ , called the *ion product*, to represent the product of the molar concentrations of the ions raised to the power of their stoichiometric coefficients. Thus, for an aqueous solution containing  $\text{Ag}^+$  and  $\text{Cl}^-$  ions at  $25^\circ\text{C}$ ,

$$Q = [\text{Ag}^+]_0[\text{Cl}^-]_0$$

The subscript 0 reminds us that these are initial concentrations and do not necessarily correspond to those at equilibrium. The possible relationships between  $Q$  and  $K_{sp}$  are

$$\begin{aligned} Q &< K_{sp} \\ [\text{Ag}^+]_0[\text{Cl}^-]_0 &< 1.6 \times 10^{-10} \end{aligned}$$

Unsaturated solution

Look up the  $K_{sp}$  value for  $\text{AgCl}$  in Table 17.2.

$$\begin{aligned} Q &= K_{sp} \\ [\text{Ag}^+][\text{Cl}^-] &= 1.6 \times 10^{-10} \end{aligned}$$

Saturated solution

$$\begin{aligned} Q &> K_{sp} \\ [\text{Ag}^+]_0[\text{Cl}^-]_0 &> 1.6 \times 10^{-10} \end{aligned}$$

Supersaturated solution;  $\text{AgCl}$  will precipitate out until the product of the ionic concentrations is equal to  $1.6 \times 10^{-10}$

## Molar Solubility and Solubility

The value of  $K_{sp}$  indicates the solubility of an ionic compound—the smaller the value, the less soluble the compound in water. However, in using  $K_{sp}$  values to compare solubilities, you should choose compounds that have similar formulas, such as  $\text{AgCl}$  and  $\text{ZnS}$ , or  $\text{CaF}_2$  and  $\text{Fe}(\text{OH})_2$ . There are two other quantities that express a substance's solubility: **molar solubility**, which is the number of moles of solute in 1 L of a saturated solution (moles per liter), and **solubility**, which is the number of grams of solute in 1 L of a saturated solution (grams per liter). Note that all these expressions refer to the concentration of saturated solutions at some given temperature (usually  $25^\circ\text{C}$ ). Figure 17.9 shows the relationships among solubility, molar solubility, and  $K_{sp}$ .

Both molar solubility and solubility are convenient to use in the laboratory. We can use them to determine  $K_{sp}$  by following the steps outlined in Figure 17.9(a).



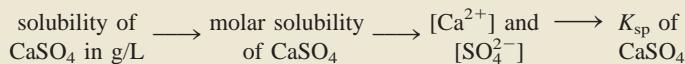
Calcium sulfate is used as a drying agent and in the manufacture of paints, ceramics, and paper. A hydrated form of calcium sulfate, called plaster of Paris, is used to make casts for broken bones.

### Example 17.6

The solubility of calcium sulfate ( $\text{CaSO}_4$ ) is found to be 0.67 g/L. Calculate the value of  $K_{sp}$  for calcium sulfate.

(Continued)

**Strategy** We are given the solubility of  $\text{CaSO}_4$  and asked to calculate its  $K_{\text{sp}}$ . The sequence of conversion steps, according to Figure 17.9(a), is



**Solution** Consider the dissociation of  $\text{CaSO}_4$  in water. Let  $s$  be the molar solubility (in mol/L) of  $\text{CaSO}_4$ .

|                      |                      |                      |                          |
|----------------------|----------------------|----------------------|--------------------------|
| $\text{CaSO}_4(s)$   | $\rightleftharpoons$ | $\text{Ca}^{2+}(aq)$ | $+ \text{SO}_4^{2-}(aq)$ |
| Initial ( $M$ ):     |                      | 0                    | 0                        |
| Change ( $M$ ):      | $-s$                 | $+s$                 | $+s$                     |
| Equilibrium ( $M$ ): |                      | $s$                  | $s$                      |

The solubility product for  $\text{CaSO}_4$  is

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = s^2$$

First we calculate the number of moles of  $\text{CaSO}_4$  dissolved in 1 L of solution

$$\frac{0.67 \text{ g CaSO}_4}{1 \text{ L soln}} \times \frac{1 \text{ mol CaSO}_4}{136.2 \text{ g CaSO}_4} = 4.9 \times 10^{-3} \text{ mol/L} = s$$

From the solubility equilibrium we see that for every mole of  $\text{CaSO}_4$  that dissolves, 1 mole of  $\text{Ca}^{2+}$  and 1 mole of  $\text{SO}_4^{2-}$  are produced. Thus, at equilibrium

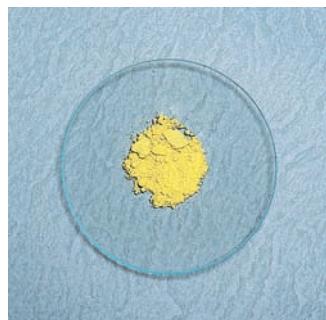
$$[\text{Ca}^{2+}] = 4.9 \times 10^{-3} M \quad \text{and} \quad [\text{SO}_4^{2-}] = 4.9 \times 10^{-3} M$$

Now we can calculate  $K_{\text{sp}}$ :

$$\begin{aligned} K_{\text{sp}} &= [\text{Ca}^{2+}][\text{SO}_4^{2-}] \\ &= (4.9 \times 10^{-3})(4.9 \times 10^{-3}) \\ &= 2.4 \times 10^{-5} \end{aligned}$$

**Similar problem:** 17.37.

**Practice Exercise** The solubility of lead chromate ( $\text{PbCrO}_4$ ) is  $4.5 \times 10^{-5}$  g/L. Calculate the solubility product of this compound.



Silver bromide is used in photographic emulsions.

Sometimes we are given the value of  $K_{\text{sp}}$  for a compound and asked to calculate the compound's molar solubility. For example, the  $K_{\text{sp}}$  of silver bromide ( $\text{AgBr}$ ) is  $7.7 \times 10^{-13}$ . We can calculate its molar solubility by the same procedure as outlined for acid ionization constants. First, we identify the species present at equilibrium. Here we have  $\text{Ag}^+$  and  $\text{Br}^-$  ions. Let  $s$  be the molar solubility (in mol/L) of  $\text{AgBr}$ . Because one unit of  $\text{AgBr}$  yields one  $\text{Ag}^+$  and one  $\text{Br}^-$  ion, at equilibrium both  $[\text{Ag}^+]$  and  $[\text{Br}^-]$  are equal to  $s$ . We summarize the changes in concentrations as follows:

|                      |                      |                   |                     |
|----------------------|----------------------|-------------------|---------------------|
| $\text{AgBr}(s)$     | $\rightleftharpoons$ | $\text{Ag}^+(aq)$ | $+ \text{Br}^-(aq)$ |
| Initial ( $M$ ):     |                      | 0.00              | 0.00                |
| Change ( $M$ ):      | $-s$                 | $+s$              | $+s$                |
| Equilibrium ( $M$ ): |                      | $s$               | $s$                 |

From Table 17.2 we write

$$\begin{aligned} K_{\text{sp}} &= [\text{Ag}^+][\text{Br}^-] \\ 7.7 \times 10^{-13} &= (s)(s) \\ s &= \sqrt{7.7 \times 10^{-13}} = 8.8 \times 10^{-7} M \end{aligned}$$

Therefore, at equilibrium

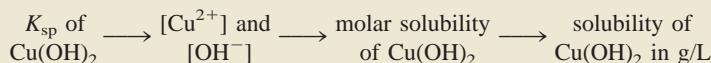
$$\begin{aligned} [\text{Ag}^+] &= 8.8 \times 10^{-7} M \\ [\text{Br}^-] &= 8.8 \times 10^{-7} M \end{aligned}$$

Thus, the molar solubility of  $\text{AgBr}$  also is  $8.8 \times 10^{-7} M$ . Knowing the molar solubility will enable us to calculate the solubility in g/L, as shown in Example 17.7.

### Example 17.7

Using the data in Table 17.2, calculate the solubility of copper(II) hydroxide,  $\text{Cu}(\text{OH})_2$ , in g/L.

**Strategy** We are given the  $K_{\text{sp}}$  of  $\text{Cu}(\text{OH})_2$  and asked to calculate its solubility in g/L. The sequence of conversion steps, according to Figure 17.9(b), is



**Solution** Consider the dissociation of  $\text{Cu}(\text{OH})_2$  in water:

|                  |  |    |     |
|------------------|--|----|-----|
|                  | $\text{Cu}(\text{OH})_2(s) \rightleftharpoons \text{Cu}^{2+}(aq) + 2\text{OH}^-(aq)$ |    |     |
| Initial (M):     |  | 0  | 0   |
| Change (M):      | -s   | +s | +2s |
| Equilibrium (M): |  | s  | 2s  |

Note that the molar concentration of  $\text{OH}^-$  is twice that of  $\text{Cu}^{2+}$ . The solubility product of  $\text{Cu}(\text{OH})_2$  is

$$\begin{aligned} K_{\text{sp}} &= [\text{Cu}^{2+}][\text{OH}^-]^2 \\ &= (s)(2s)^2 = 4s^3 \end{aligned}$$

From the  $K_{\text{sp}}$  value in Table 17.2, we solve for the molar solubility of  $\text{Cu}(\text{OH})_2$  as follows:

$$\begin{aligned} 2.2 \times 10^{-20} &= 4s^3 \\ s^3 &= \frac{2.2 \times 10^{-20}}{4} = 5.5 \times 10^{-21} \end{aligned}$$

Hence

$$s = 1.8 \times 10^{-7} M$$

Finally, from the molar mass of  $\text{Cu}(\text{OH})_2$  and its molar solubility, we calculate the solubility in g/L:

$$\begin{aligned} \text{solubility of Cu(OH)}_2 &= \frac{1.8 \times 10^{-7} \text{ mol Cu(OH)}_2}{1 \text{ L soln}} \times \frac{97.57 \text{ g Cu(OH)}_2}{1 \text{ mol Cu(OH)}_2} \\ &= 1.8 \times 10^{-5} \text{ g/L} \end{aligned}$$



Copper(II) hydroxide is used as a pesticide and to treat seeds.

**Practice Exercise** Calculate the solubility of silver chloride ( $\text{AgCl}$ ) in g/L.

**Similar problem: 17.38.**

As Examples 17.6 and 17.7 show, solubility and solubility product are related. If we know one, we can calculate the other, but each quantity provides different information. Table 17.3 shows the relationship between molar solubility and solubility product for a number of ionic compounds.

When carrying out solubility and/or solubility product calculations, keep in mind these important points:

**TABLE 17.3** Relationship Between  $K_{\text{sp}}$  and Molar Solubility ( $s$ )

| Compound  | $K_{\text{sp}}$ Expression               | Cation | Anion | Relation Between $K_{\text{sp}}$ and $s$   |
|---|--|--------|-------|--|
| AgCl  | $[\text{Ag}^+][\text{Cl}^-]$             | $s$    | $s$   | $K_{\text{sp}} = s^2; s = (K_{\text{sp}})^{\frac{1}{2}}$                           |
| BaSO <sub>4</sub>                               | $[\text{Ba}^{2+}][\text{SO}_4^{2-}]$     | $s$    | $s$   | $K_{\text{sp}} = s^2; s = (K_{\text{sp}})^{\frac{1}{2}}$                           |
| Ag <sub>2</sub> CO <sub>3</sub>                 | $[\text{Ag}^+]^2[\text{CO}_3^{2-}]$      | $2s$   | $s$   | $K_{\text{sp}} = 4s^3; s = \left(\frac{K_{\text{sp}}}{4}\right)^{\frac{1}{3}}$     |
| PbF <sub>2</sub>                                | $[\text{Pb}^{2+}][\text{F}^-]^2$         | $s$    | $2s$  | $K_{\text{sp}} = 4s^3; s = \left(\frac{K_{\text{sp}}}{4}\right)^{\frac{1}{3}}$     |
| Al(OH) <sub>3</sub>                             | $[\text{Al}^{3+}][\text{OH}^-]^3$        | $s$    | $3s$  | $K_{\text{sp}} = 27s^4; s = \left(\frac{K_{\text{sp}}}{27}\right)^{\frac{1}{4}}$   |
| Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> | $[\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$ | $3s$   | $2s$  | $K_{\text{sp}} = 108s^5; s = \left(\frac{K_{\text{sp}}}{108}\right)^{\frac{1}{5}}$ |

- The solubility is the quantity of a substance that dissolves in a certain quantity of water. In solubility equilibria calculations, it is usually expressed as *grams* of solute per liter of solution. Molar solubility is the number of *moles* of solute per liter of solution.
- The solubility product is an equilibrium constant.
- Molar solubility, solubility, and solubility product all refer to a *saturated solution*.

## Predicting Precipitation Reactions



A kidney stone.

From a knowledge of the solubility rules (see Section 4.2) and the solubility products listed in Table 17.2, we can predict whether a precipitate will form when we mix two solutions or add a soluble compound to a solution. This ability often has practical value. In industrial and laboratory preparations, we can adjust the concentrations of ions until the ion product exceeds  $K_{\text{sp}}$  in order to obtain a given compound (in the form of a precipitate). The ability to predict precipitation reactions is also useful in medicine. For example, kidney stones, which can be extremely painful, consist largely of calcium oxalate,  $\text{CaC}_2\text{O}_4$  ( $K_{\text{sp}} = 2.3 \times 10^{-9}$ ). The normal physiological concentration of calcium ions in blood plasma is about 5 mM (1 mM =  $1 \times 10^{-3}$  M). Oxalate ions ( $\text{C}_2\text{O}_4^{2-}$ ), derived from oxalic acid present in many vegetables such as rhubarb and spinach, react with the calcium ions to form insoluble calcium oxalate, which can gradually build up in the kidneys. Proper adjustment of a patient's diet can help to reduce precipitate formation.

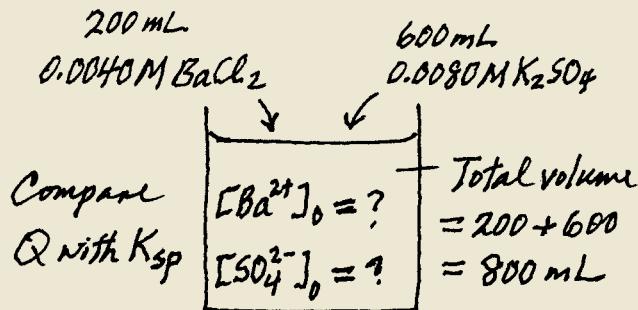
### Example 17.8

Exactly 200 mL of 0.0040 M  $\text{BaCl}_2$  are added to exactly 600 mL of 0.0080 M  $\text{K}_2\text{SO}_4$ . Will a precipitate form?

**Strategy** Under what condition will an ionic compound precipitate from solution? The ions in solution are  $\text{Ba}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ , and  $\text{SO}_4^{2-}$ . According to the solubility rules listed in Table 4.2 (p. 98), the only precipitate that can form is  $\text{BaSO}_4$ . From the information given, we can calculate  $[\text{Ba}^{2+}]$  and  $[\text{SO}_4^{2-}]$  because we know the number of moles of the ions in the original solutions and the volume of the combined solution. Next we calculate the reaction quotient  $Q$  ( $Q = [\text{Ba}^{2+}]_0[\text{SO}_4^{2-}]_0$ ) and compare the value of  $Q$

(Continued)

with  $K_{\text{sp}}$  of  $\text{BaSO}_4$  to see if a precipitate will form, that is, if the solution is supersaturated. It is helpful to make a sketch of the situation.



**Solution** The number of moles of  $\text{Ba}^{2+}$  present in the original 200 mL of solution is

$$200 \text{ mL} \times \frac{0.0040 \text{ mol Ba}^{2+}}{1 \text{ L soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 8.0 \times 10^{-4} \text{ mol Ba}^{2+}$$

The total volume after combining the two solutions is 800 mL. The concentration of  $\text{Ba}^{2+}$  in the 800 mL volume is

$$\begin{aligned} [\text{Ba}^{2+}] &= \frac{8.0 \times 10^{-4} \text{ mol}}{800 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L soln}} \\ &= 1.0 \times 10^{-3} \text{ M} \end{aligned}$$

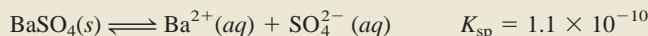
The number of moles of  $\text{SO}_4^{2-}$  in the original 600 mL solution is

$$600 \text{ mL} \times \frac{0.0080 \text{ mol SO}_4^{2-}}{1 \text{ L soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 4.8 \times 10^{-3} \text{ mol SO}_4^{2-}$$

The concentration of  $\text{SO}_4^{2-}$  in the 800 mL of the combined solution is

$$\begin{aligned} [\text{SO}_4^{2-}] &= \frac{4.8 \times 10^{-3} \text{ mol}}{800 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L soln}} \\ &= 6.0 \times 10^{-3} \text{ M} \end{aligned}$$

Now we must compare  $Q$  with  $K_{\text{sp}}$ . From Table 17.2,



As for  $Q$ ,

$$\begin{aligned} Q &= [\text{Ba}^{2+}]_0[\text{SO}_4^{2-}]_0 = (1.0 \times 10^{-3})(6.0 \times 10^{-3}) \\ &= 6.0 \times 10^{-6} \end{aligned}$$

Therefore,

$$Q > K_{\text{sp}}$$

The solution is supersaturated because the value of  $Q$  indicates that the concentrations of the ions are too large. Thus, some of the  $\text{BaSO}_4$  will precipitate out of solution until

$$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10}$$

**Similar problem: 17.41.**

**Practice Exercise** If 2.00 mL of 0.200 M NaOH are added to 1.00 L of 0.100 M  $\text{CaCl}_2$ , will precipitation occur?

## 17.6 The Common Ion Effect and Solubility

As we have noted, the solubility product is an equilibrium constant; precipitation of an ionic compound from solution occurs whenever the ion product exceeds  $K_{\text{sp}}$  for that substance. In a saturated solution of AgCl, for example, the ion product  $[\text{Ag}^+][\text{Cl}^-]$  is, of course, equal to  $K_{\text{sp}}$ . Furthermore, simple stoichiometry tells us that  $[\text{Ag}^+] = [\text{Cl}^-]$ . But this equality does not hold in all situations.

Suppose we study a solution containing two dissolved substances that share a common ion, say, AgCl and AgNO<sub>3</sub>. In addition to the dissociation of AgCl, the following process also contributes to the total concentration of the common silver ions in solution:



If AgNO<sub>3</sub> is added to a saturated AgCl solution, the increase in [Ag<sup>+</sup>] will make the ion product greater than the solubility product:

$$Q = [\text{Ag}^+]_0[\text{Cl}^-]_0 > K_{\text{sp}}$$

**At a given temperature, only the solubility of a compound is altered (decreased) by the common ion effect. Its solubility product, which is an equilibrium constant, remains the same whether or not other substances are present in the solution.**

To reestablish equilibrium, some AgCl will precipitate out of the solution, as Le Châtelier's principle would predict, until the ion product is once again equal to  $K_{\text{sp}}$ . The effect of adding a common ion, then, is a *decrease* in the solubility of the salt (AgCl) in solution. Note that in this case [Ag<sup>+</sup>] is no longer equal to [Cl<sup>-</sup>] at equilibrium; rather, [Ag<sup>+</sup>] > [Cl<sup>-</sup>].

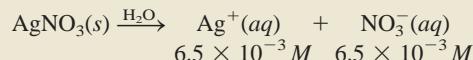
### Example 17.9

Calculate the solubility of silver chloride (in g/L) in a  $6.5 \times 10^{-3} M$  silver nitrate solution.

**Strategy** This is a common-ion problem. The common ion here is Ag<sup>+</sup>, which is supplied by both AgCl and AgNO<sub>3</sub>. Remember that the presence of the common ion will affect only the solubility of AgCl (in g/L), but not the  $K_{\text{sp}}$  value because it is an equilibrium constant.

**Solution** *Step 1:* The relevant species in solution are Ag<sup>+</sup> ions (from both AgCl and AgNO<sub>3</sub>) and Cl<sup>-</sup> ions. The NO<sub>3</sub><sup>-</sup> ions are spectator ions.

*Step 2:* Because AgNO<sub>3</sub> is a soluble strong electrolyte, it dissociates completely:



Let  $s$  be the molar solubility of AgCl in AgNO<sub>3</sub> solution. We summarize the changes in concentrations as follows:

|                  |                            |                      |                      |                     |
|------------------|----------------------------|----------------------|----------------------|---------------------|
| Initial (M):     | $\text{AgCl}(s)$           | $\rightleftharpoons$ | $\text{Ag}^+(aq)$    | $+ \text{Cl}^-(aq)$ |
| Change (M):      | $-s$                       |                      | $6.5 \times 10^{-3}$ | 0.00                |
| Equilibrium (M): | $(6.5 \times 10^{-3} + s)$ |                      | $+s$                 | $+s$                |

*Step 3:*

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

$$1.6 \times 10^{-10} = (6.5 \times 10^{-3} + s)(s)$$

(Continued)

Because  $\text{AgCl}$  is quite insoluble and the presence of  $\text{Ag}^+$  ions from  $\text{AgNO}_3$  further lowers the solubility of  $\text{AgCl}$ ,  $s$  must be very small compared with  $6.5 \times 10^{-3}$ . Therefore, applying the approximation  $6.5 \times 10^{-3} + s \approx 6.5 \times 10^{-3}$ , we obtain

$$\begin{aligned} 1.6 \times 10^{-10} &= (6.5 \times 10^{-3})s \\ s &= 2.5 \times 10^{-8} \text{ M} \end{aligned}$$

*Step 4:* At equilibrium,

$$\begin{aligned} [\text{Ag}^+] &= (6.5 \times 10^{-3} + 2.5 \times 10^{-8}) \text{ M} \approx 6.5 \times 10^{-3} \text{ M} \\ [\text{Cl}^-] &= 2.5 \times 10^{-8} \text{ M} \end{aligned}$$

and so our approximation was justified in Step 3. Because all the  $\text{Cl}^-$  ions must come from  $\text{AgCl}$ , the amount of  $\text{AgCl}$  dissolved in  $\text{AgNO}_3$  solution also is  $2.5 \times 10^{-8} \text{ M}$ . Then, knowing the molar mass of  $\text{AgCl}$  (143.4 g), we can calculate the solubility of  $\text{AgCl}$  as follows:

$$\begin{aligned} \text{solubility of AgCl in AgNO}_3 \text{ solution} &= \frac{2.5 \times 10^{-8} \text{ mol AgCl}}{1 \text{ L soln}} \times \frac{143.4 \text{ g AgCl}}{1 \text{ mol AgCl}} \\ &= 3.6 \times 10^{-6} \text{ g/L} \end{aligned}$$

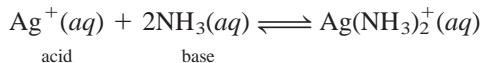
**Check** The solubility of  $\text{AgCl}$  in pure water is  $1.9 \times 10^{-3} \text{ g/L}$  (see the Practice Exercise in Example 17.7). Therefore, the lower solubility ( $3.6 \times 10^{-6} \text{ g/L}$ ) in the presence of  $\text{AgNO}_3$  is reasonable. You should also be able to predict the lower solubility using Le Châtelier's principle. Adding  $\text{Ag}^+$  ions shifts the solubility equilibrium to the left, thus decreasing the solubility of  $\text{AgCl}$ .

**Similar problem: 17.46.**

**Practice Exercise** Calculate the solubility in g/L of  $\text{AgBr}$  in (a) pure water and in (b) 0.0010 M  $\text{NaBr}$ .

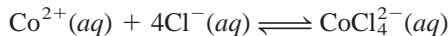
## 17.7 Complex Ion Equilibria and Solubility

Lewis acid-base reactions in which a metal cation (electron-pair acceptor) combines with a Lewis base (electron-pair donor) result in the formation of complex ions:

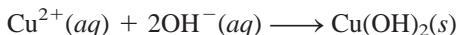


Thus, we can define a **complex ion** as an ion containing a central metal cation bonded to one or more molecules or ions. Complex ions are crucial to many chemical and biological processes. Here we will consider the effect of complex ion formation on solubility. In Chapter 20 we will discuss the chemistry of complex ions in more detail.

Transition metals have a particular tendency to form complex ions. For example, a solution of cobalt(II) chloride is pink because of the presence of the  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  ions (Figure 17.10). When  $\text{HCl}$  is added, the solution turns blue as a result of the formation of the complex ion  $\text{CoCl}_4^{2-}$ :



Copper(II) sulfate ( $\text{CuSO}_4$ ) dissolves in water to produce a blue solution. The hydrated copper(II) ions are responsible for this color; many other sulfates ( $\text{Na}_2\text{SO}_4$ , for example) are colorless. Adding a few drops of concentrated ammonia solution to a  $\text{CuSO}_4$  solution causes a light-blue precipitate, copper(II) hydroxide, to form (Figure 17.11):



Lewis acids and bases are discussed in Section 16.11.

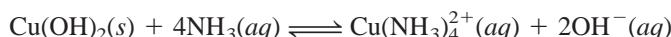
According to our definition,  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  itself is a complex ion. When we write  $\text{Co}(\text{H}_2\text{O})_6^{2+}$ , we mean the hydrated  $\text{Co}^{2+}$  ion.

**Figure 17.10**

(Left) An aqueous cobalt(II) chloride solution. The pink color is due to the presence of  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  ions. (Right) After the addition of HCl solution, the solution turns blue because of the formation of the complex  $\text{CoCl}_4^{2-}$  ions.



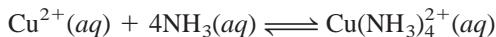
in which the  $\text{OH}^-$  ions are supplied by the ammonia solution. If an excess of  $\text{NH}_3$  is then added, the blue precipitate redissolves to produce a beautiful dark-blue solution, this time as a result of the formation of the complex ion  $\text{Cu}(\text{NH}_3)_4^{2+}$ , also shown in Figure 17.11:



Thus, the formation of the complex ion  $\text{Cu}(\text{NH}_3)_4^{2+}$  increases the solubility of  $\text{Cu}(\text{OH})_2$ .

A measure of the tendency of a metal ion to form a particular complex ion is given by the **formation constant**  $K_f$  (also called the **stability constant**), which is the equilibrium constant for complex ion formation. The larger  $K_f$  is, the more stable the complex ion is. Table 17.4 lists the formation constants of a number of complex ions.

The formation of the  $\text{Cu}(\text{NH}_3)_4^{2+}$  ion can be expressed as



for which the formation constant is

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} \\ = 5.0 \times 10^{13}$$

The very large value of  $K_f$  in this case indicates the great stability of the complex ion in solution and accounts for the very low concentration of copper(II) ions at equilibrium.

**Figure 17.11**

Left: An aqueous solution of copper(II) sulfate. Center: After the addition of a few drops of a concentrated aqueous ammonia solution, a light-blue precipitate of  $\text{Cu}(\text{OH})_2$  is formed. Right: When more concentrated aqueous ammonia solution is added, the  $\text{Cu}(\text{OH})_2$  precipitate dissolves to form the dark-blue complex ion  $\text{Cu}(\text{NH}_3)_4^{2+}$ .



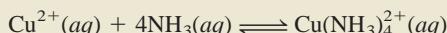
**TABLE 17.4** Formation Constants of Selected Complex Ions in Water at 25°C

| Complex Ion                     | Equilibrium Expression   | Formation Constant ( $K_f$ ) |
|---------------------------------|--|------------------------------|
| $\text{Ag}(\text{NH}_3)_2^+$    | $\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+$       | $1.5 \times 10^7$            |
| $\text{Ag}(\text{CN})_2^-$      | $\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons \text{Ag}(\text{CN})_2^-$         | $1.0 \times 10^{21}$         |
| $\text{Cu}(\text{CN})_4^{2-}$   | $\text{Cu}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Cu}(\text{CN})_4^{2-}$   | $1.0 \times 10^{25}$         |
| $\text{Cu}(\text{NH}_3)_4^{2+}$ | $\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}$ | $5.0 \times 10^{13}$         |
| $\text{Cd}(\text{CN})_4^{2-}$   | $\text{Cd}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Cd}(\text{CN})_4^{2-}$   | $7.1 \times 10^{16}$         |
| $\text{CdI}_4^{2-}$             | $\text{Cd}^{2+} + 4\text{I}^- \rightleftharpoons \text{CdI}_4^{2-}$              | $2.0 \times 10^6$            |
| $\text{HgCl}_4^{2-}$            | $\text{Hg}^{2+} + 4\text{Cl}^- \rightleftharpoons \text{HgCl}_4^{2-}$            | $1.7 \times 10^{16}$         |
| $\text{HgI}_4^{2-}$             | $\text{Hg}^{2+} + 4\text{I}^- \rightleftharpoons \text{HgI}_4^{2-}$              | $2.0 \times 10^{30}$         |
| $\text{Hg}(\text{CN})_4^{2-}$   | $\text{Hg}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Hg}(\text{CN})_4^{2-}$   | $2.5 \times 10^{41}$         |
| $\text{Co}(\text{NH}_3)_6^{3+}$ | $\text{Co}^{3+} + 6\text{NH}_3 \rightleftharpoons \text{Co}(\text{NH}_3)_6^{3+}$ | $5.0 \times 10^{31}$         |
| $\text{Zn}(\text{NH}_3)_4^{2+}$ | $\text{Zn}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Zn}(\text{NH}_3)_4^{2+}$ | $2.9 \times 10^9$            |

### Example 17.10

A 0.20-mole quantity of  $\text{CuSO}_4$  is added to a liter of 1.20 M  $\text{NH}_3$  solution. What is the concentration of  $\text{Cu}^{2+}$  ions at equilibrium?

**Strategy** The addition of  $\text{CuSO}_4$  to the  $\text{NH}_3$  solution results in complex ion formation



From Table 17.4 we see that the formation constant ( $K_f$ ) for this reaction is very large; therefore, the reaction lies mostly to the right. At equilibrium, the concentration of  $\text{Cu}^{2+}$  will be very small. As a good approximation, we can assume that essentially all the dissolved  $\text{Cu}^{2+}$  ions end up as  $\text{Cu}(\text{NH}_3)_4^{2+}$  ions. How many moles of  $\text{NH}_3$  will react with 0.20 mole of  $\text{Cu}^{2+}$ ? How many moles of  $\text{Cu}(\text{NH}_3)_4^{2+}$  will be produced? A very small amount of  $\text{Cu}^{2+}$  will be present at equilibrium. Set up the  $K_f$  expression for the preceding equilibrium to solve for  $[\text{Cu}^{2+}]$ .

**Solution** The amount of  $\text{NH}_3$  consumed in forming the complex ion is  $4 \times 0.20 \text{ mol}$ , or 0.80 mol. (Note that 0.20 mol  $\text{Cu}^{2+}$  is initially present in solution and four  $\text{NH}_3$  molecules are needed to form a complex ion with one  $\text{Cu}^{2+}$  ion.) The concentration of  $\text{NH}_3$  at equilibrium is therefore  $(1.20 - 0.80) \text{ mol/L}$  soln or 0.40 M, and that of  $\text{Cu}(\text{NH}_3)_4^{2+}$  is 0.20 mol/L soln or 0.20 M, the same as the initial concentration of  $\text{Cu}^{2+}$ . [There is a 1:1 mole ratio between  $\text{Cu}^{2+}$  and  $\text{Cu}(\text{NH}_3)_4^{2+}$ .] Because  $\text{Cu}(\text{NH}_3)_4^{2+}$  does dissociate to a slight extent, we call the concentration of  $\text{Cu}^{2+}$  at equilibrium  $x$  and write

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}$$

$$5.0 \times 10^{13} = \frac{0.20}{x(0.40)^4}$$

Solving for  $x$  and keeping in mind that the volume of the solution is 1 L, we obtain

$$x = [\text{Cu}^{2+}] = 1.6 \times 10^{-13} \text{ M}$$

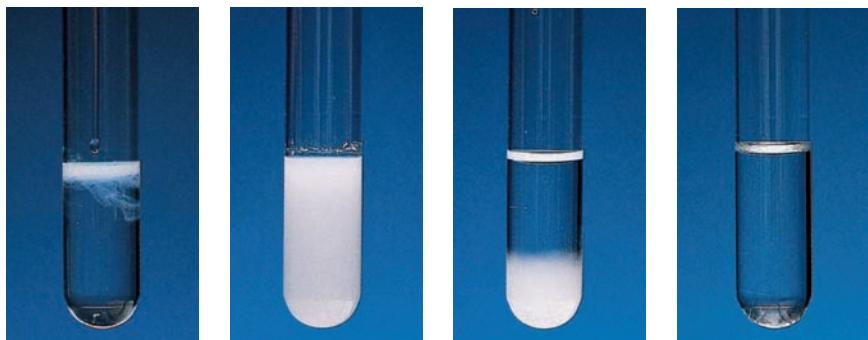
The very small value of  $[\text{Cu}^{2+}]$  justifies our approximation.

**Practice Exercise** If 2.50 g of  $\text{CuSO}_4$  are dissolved in  $9.0 \times 10^2 \text{ mL}$  of 0.30 M  $\text{NH}_3$ , what are the concentrations of  $\text{Cu}^{2+}$ ,  $\text{Cu}(\text{NH}_3)_4^{2+}$ , and  $\text{NH}_3$  at equilibrium?

Similar problem: 17.53.

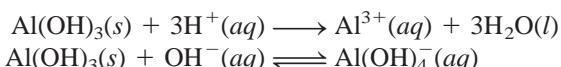
**Figure 17.12**

(Left to right) Formation of  $\text{Al(OH)}_3$  precipitate when  $\text{NaOH}$  solution is added to an  $\text{Al}(\text{NO}_3)_3$  solution. With further addition of  $\text{NaOH}$  solution, the precipitate dissolves due to the formation of the complex ion  $\text{Al(OH)}_4^-$ .



**All amphoteric hydroxides are insoluble compounds.**

Finally, we note that there is a class of hydroxides, called *amphoteric hydroxides*, which can react with both acids and bases. Examples are  $\text{Al(OH)}_3$ ,  $\text{Pb(OH)}_2$ ,  $\text{Cr(OH)}_3$ ,  $\text{Zn(OH)}_2$ , and  $\text{Cd(OH)}_2$ . For example, aluminum hydroxide reacts with acids and bases as:



The increase in solubility of  $\text{Al(OH)}_3$  in a basic medium is the result of the formation of the complex ion  $[\text{Al(OH)}_4^-]$  in which  $\text{Al(OH)}_3$  acts as the Lewis acid and  $\text{OH}^-$  acts as the Lewis base (Figure 17.12). Other amphoteric hydroxides behave in a similar manner.

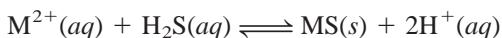
## 17.8 Application of the Solubility Product Principle to Qualitative Analysis

In Section 4.6, we discussed the principle of gravimetric analysis, by which we measure the amount of an ion in an unknown sample. Here we will briefly discuss *qualitative analysis, the determination of the types of ions present in a solution*. We will focus on the cations.

**Do not confuse the groups in Table 17.5, which are based on solubility products, with those in the periodic table, which are based on the electron configurations of the elements.**

Twenty common cations can be analyzed readily in aqueous solution. These cations can be divided into five groups according to the solubility products of their insoluble salts (Table 17.5). Because an unknown solution may contain any one or up to all 20 ions, analysis must be carried out systematically from group 1 through group 5. Let us consider the general procedure for separating these ions by adding precipitating reagents to an unknown solution.

- *Group 1 cations.* When dilute HCl is added to the unknown solution, only the  $\text{Ag}^+$ ,  $\text{Hg}_2^{2+}$ , and  $\text{Pb}^{2+}$  ions precipitate as insoluble chlorides. The other ions, whose chlorides are soluble, remain in solution.
- *Group 2 cations.* After the chloride precipitates have been removed by filtration, hydrogen sulfide is reacted with the unknown acidic solution. Under this condition, the concentration of the  $\text{S}^{2-}$  ion in solution is negligible. Therefore, the precipitation of metal sulfides is best represented as



**TABLE 17.5** Separation of Cations into Groups According to Their Precipitation Reactions with Various Reagents

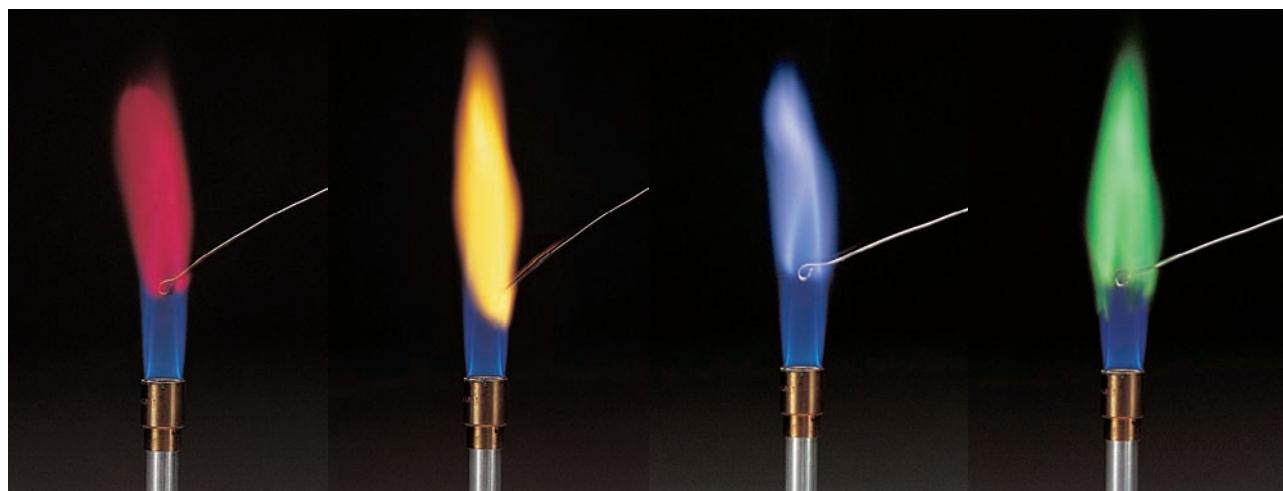
| Group | Cation             | Precipitating Reagents                     | Insoluble Compound       | $K_{sp}$              |
|-------|--------------------|--|--------------------------|-----------------------|
| 1     | $\text{Ag}^+$      | HCl  | AgCl                     | $1.6 \times 10^{-10}$ |
|       | $\text{Hg}_2^{2+}$ |  | $\text{Hg}_2\text{Cl}_2$ | $3.5 \times 10^{-18}$ |
|       | $\text{Pb}^{2+}$   |  | $\text{PbCl}_2$          | $2.4 \times 10^{-4}$  |
| 2     | $\text{Bi}^{3+}$   | H <sub>2</sub> S<br>in acidic<br>solutions | $\text{Bi}_2\text{S}_3$  | $1.6 \times 10^{-72}$ |
|       | $\text{Cd}^{2+}$   |  | CdS                      | $8.0 \times 10^{-28}$ |
|       | $\text{Cu}^{2+}$   |  | CuS                      | $6.0 \times 10^{-37}$ |
|       | $\text{Hg}^{2+}$   |  | HgS                      | $4.0 \times 10^{-54}$ |
|       | $\text{Sn}^{2+}$   |  | SnS                      | $1.0 \times 10^{-26}$ |
| 3     | $\text{Al}^{3+}$   | H <sub>2</sub> S<br>in basic<br>solutions  | $\text{Al(OH)}_3$        | $1.8 \times 10^{-33}$ |
|       | $\text{Co}^{2+}$   |  | CoS                      | $4.0 \times 10^{-21}$ |
|       | $\text{Cr}^{3+}$   |  | $\text{Cr(OH)}_3$        | $3.0 \times 10^{-29}$ |
|       | $\text{Fe}^{2+}$   |  | FeS                      | $6.0 \times 10^{-19}$ |
|       | $\text{Mn}^{2+}$   |  | MnS                      | $3.0 \times 10^{-14}$ |
|       | $\text{Ni}^{2+}$   |  | NiS                      | $1.4 \times 10^{-24}$ |
|       | $\text{Zn}^{2+}$   |  | ZnS                      | $3.0 \times 10^{-23}$ |
| 4     | $\text{Ba}^{2+}$   | Na <sub>2</sub> CO <sub>3</sub>            | BaCO <sub>3</sub>        | $8.1 \times 10^{-9}$  |
|       | $\text{Ca}^{2+}$   |  | CaCO <sub>3</sub>        | $8.7 \times 10^{-9}$  |
|       | $\text{Sr}^{2+}$   |  | SrCO <sub>3</sub>        | $1.6 \times 10^{-9}$  |
| 5     | $\text{K}^+$       | No precipitating<br>reagent                | None                     |                       |
|       | $\text{Na}^+$      |  | None                     |                       |
|       | $\text{NH}_4^+$    |  | None                     |                       |

Adding acid to the solution shifts this equilibrium to the left so that only the least soluble metal sulfides, that is, those with the smallest  $K_{sp}$  values, will precipitate out of solution. These are Bi<sub>2</sub>S<sub>3</sub>, CdS, CuS, HgS, and SnS.

- **Group 3 cations.** At this stage, sodium hydroxide is added to the solution to make it basic. In a basic solution, the preceding equilibrium shifts to the right. Therefore, the more soluble sulfides (CoS, FeS, MnS, NiS, and ZnS) now precipitate out of solution. Note that the Al<sup>3+</sup> and Cr<sup>3+</sup> ions actually precipitate as the hydroxides Al(OH)<sub>3</sub> and Cr(OH)<sub>3</sub>, rather than as the sulfides, because the hydroxides are less soluble. The solution is then filtered to remove the insoluble sulfides and hydroxides.
- **Group 4 cations.** After all the group 1, 2, and 3 cations have been removed from solution, sodium carbonate is added to the basic solution to precipitate Ba<sup>2+</sup>, Ca<sup>2+</sup>, and Sr<sup>2+</sup> ions as BaCO<sub>3</sub>, CaCO<sub>3</sub>, and SrCO<sub>3</sub>. These precipitates too are removed from solution by filtration.
- **Group 5 cations.** At this stage, the only cations possibly remaining in solution are Na<sup>+</sup>, K<sup>+</sup>, and NH<sub>4</sub><sup>+</sup>. The presence of NH<sub>4</sub><sup>+</sup> can be determined by adding sodium hydroxide:



The ammonia gas is detected either by noting its characteristic odor or by observing a piece of wet red litmus paper turning blue when placed above (not in contact

**Figure 17.13**

Left to right: Flame colors of lithium, sodium, potassium, and copper.

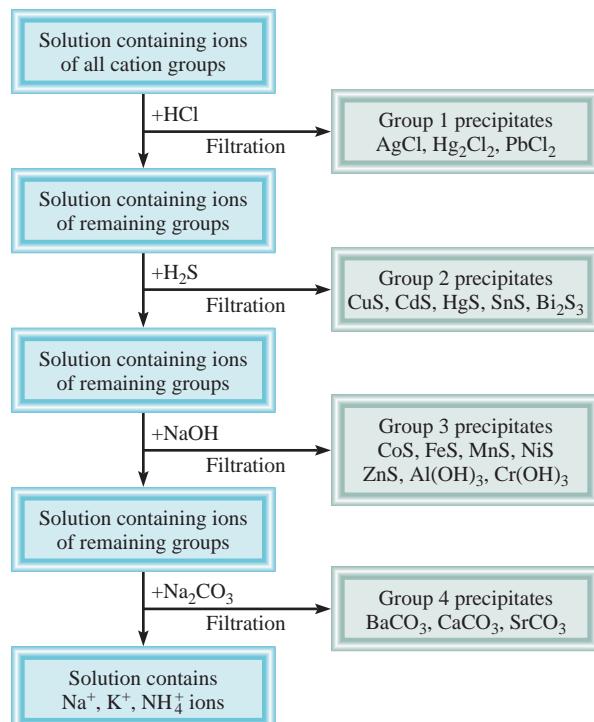
**Because NaOH is added in group 3 and Na<sub>2</sub>CO<sub>3</sub> is added in group 4, the flame test for Na<sup>+</sup> ions is carried out using the original solution.**

with) the solution. To confirm the presence of Na<sup>+</sup> and K<sup>+</sup> ions, we usually use a flame test, as follows: A piece of platinum wire (chosen because platinum is inert) is moistened with the solution and is then held over a Bunsen burner flame. Each type of metal ion gives a characteristic color when heated in this manner. For example, the color emitted by Na<sup>+</sup> ions is yellow, that of K<sup>+</sup> ions is violet, and that of Cu<sup>2+</sup> ions is green (Figure 17.13).

Figure 17.14 summarizes this scheme for separating metal ions.

**Figure 17.14**

A flow chart for the separation of cations in qualitative analysis.



Two points regarding qualitative analysis must be mentioned. First, the separation of the cations into groups is made as selective as possible; that is, the anions that are added as reagents must be such that they will precipitate the fewest types of cations. For example, all the cations in group 1 also form insoluble sulfides. Thus, if  $\text{H}_2\text{S}$  were reacted with the solution at the start, as many as seven different sulfides might precipitate out of solution (group 1 and group 2 sulfides), an undesirable outcome. Second, the removal of cations at each step must be carried out as completely as possible. For example, if we do not add enough HCl to the unknown solution to remove all the group 1 cations, they will precipitate with the group 2 cations as insoluble sulfides; this too would interfere with further chemical analysis and lead us to draw erroneous conclusions.

## KEY EQUATIONS

$$\text{p}K_{\text{a}} = -\log K_{\text{a}} \quad (17.2) \quad \text{Definition of } \text{p}K_{\text{a}}$$

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{conjugate base}]}{[\text{acid}]} \quad (17.3) \quad \text{Henderson-Hasselbalch equation.}$$

## SUMMARY OF FACTS AND CONCEPTS

1. Equilibria involving weak acids or weak bases in aqueous solution are homogeneous. Solubility equilibria are examples of heterogeneous equilibria.
2. A buffer solution is a combination of a weak acid and its weak conjugate base; the solution reacts with small amounts of added acid or base in such a way that the pH of the solution remains nearly constant. Buffer systems play a vital role in maintaining the pH of body fluids.
3. The pH at the equivalence point of an acid-base titration depends on the hydrolysis of the salt formed in the neutralization reaction. For strong acid-strong base titrations, the pH at the equivalence point is 7; for weak acid-strong base titrations, the pH at the equivalence point is greater than 7; for strong acid-weak base titrations, the pH at the equivalence point is less than 7.
4. Acid-base indicators are weak organic acids or bases that change color at the end point in an acid-base neutralization reaction.
5. The solubility product  $K_{\text{sp}}$  expresses the equilibrium between a solid and its ions in solution. Solubility can be found from  $K_{\text{sp}}$  and vice versa. The presence of a common ion decreases the solubility of a salt.
6. Complex ions are formed in solution by the combination of a metal cation with a Lewis base. The formation constant  $K_f$  measures the tendency toward the formation of a specific complex ion. Complex ion formation can increase the solubility of an insoluble substance.
7. Qualitative analysis is the identification of cations and anions in solution. It is based largely on the principles of solubility equilibria.

## KEY WORDS

Buffer solution, p. 575  
Complex ion, p. 597

End point, p. 586  
Formation constant ( $K_f$ ), p. 598

Molar solubility, p. 591  
Qualitative analysis, p. 600

Solubility, p. 591  
Solubility product ( $K_{\text{sp}}$ ), p. 590

## QUESTIONS AND PROBLEMS

### Buffer Solutions

#### Review Questions

- 17.1 Define buffer solution.
- 17.2 Define  $pK_a$  for a weak acid and explain the relationship between the value of the  $pK_a$  and the strength of the acid. Do the same for  $pK_b$  and a weak base.
- 17.3 The  $pK_{a_s}$ s of two monoprotic acids HA and HB are 5.9 and 8.1, respectively. Which of the two is the stronger acid?
- 17.4 The  $pK_b$ s for the bases  $X^-$ ,  $Y^-$ , and  $Z^-$  are 2.72, 8.66, and 4.57, respectively. Arrange the following acids in order of increasing strength: HX, HY, HZ.

#### Problems

- 17.5 Specify which of these systems can be classified as a buffer system: (a) KCl/HCl, (b)  $\text{NH}_3/\text{NH}_4\text{NO}_3$ , (c)  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$ .
- 17.6 Specify which of these systems can be classified as a buffer system: (a)  $\text{KNO}_2/\text{HNO}_2$ , (b)  $\text{KHSO}_4/\text{H}_2\text{SO}_4$ , (c)  $\text{HCOOK}/\text{HCOOH}$ .
- 17.7 The pH of a bicarbonate–carbonic acid buffer is 8.00. Calculate the ratio of the concentration of carbonic acid to that of the bicarbonate ion.
- 17.8 Calculate the pH of these two buffer solutions: (a) 2.0 M  $\text{CH}_3\text{COONa}/2.0 \text{ M CH}_3\text{COOH}$ , (b) 0.20 M  $\text{CH}_3\text{COONa}/0.20 \text{ M CH}_3\text{COOH}$ . Which is the more effective buffer? Why?
- 17.9 Calculate the pH of the buffer system 0.15 M  $\text{NH}_3/0.35 \text{ M NH}_4\text{Cl}$ .
- 17.10 What is the pH of the buffer 0.10 M  $\text{Na}_2\text{HPO}_4/0.15 \text{ M KH}_2\text{PO}_4$ ?
- 17.11 The pH of a sodium acetate–acetic acid buffer is 4.50. Calculate the ratio  $[\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}]$ .
- 17.12 The pH of blood plasma is 7.40. Assuming the principal buffer system is  $\text{HCO}_3^-/\text{H}_2\text{CO}_3$ , calculate the ratio  $[\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$ . Is this buffer more effective against an added acid or an added base?
- 17.13 Calculate the pH of 1.00 L of the buffer 0.80 M  $\text{CH}_3\text{NH}_2/1.00 \text{ M CH}_3\text{NH}_3\text{Cl}$  before and after the addition of (a) 0.070 mol NaOH and (b) 0.11 mol HCl. (See Table 16.5 for  $K_a$  value.)
- 17.14 Calculate the pH of 1.00 L of the buffer 1.00 M  $\text{CH}_3\text{COONa}/1.00 \text{ M CH}_3\text{COOH}$  before and after the addition of (a) 0.080 mol NaOH and (b) 0.12 mol HCl. (Assume that there is no change in volume.)
- 17.15 A diprotic acid,  $\text{H}_2\text{A}$ , has the following ionization constants:  $K_{a_1} = 1.1 \times 10^{-3}$  and  $K_{a_2} = 2.5 \times 10^{-6}$ . To

make up a buffer solution of pH 5.80, which combination would you choose:  $\text{NaHA}/\text{H}_2\text{A}$  or  $\text{Na}_2\text{A}/\text{NaHA}$ ?

- 17.16** A student wishes to prepare a buffer solution at pH = 8.60. Which of these weak acids should she choose and why: HA ( $K_a = 2.7 \times 10^{-3}$ ), HB ( $K_a = 4.4 \times 10^{-6}$ ), or HC ( $K_a = 2.6 \times 10^{-9}$ )?

### Acid-Base Titrations

#### Problems

- 17.17 A 0.2688-g sample of a monoprotic acid neutralizes 16.4 mL of 0.08133 M KOH solution. Calculate the molar mass of the acid.
- 17.18 A 5.00-g quantity of a diprotic acid is dissolved in water and made up to exactly 250 mL. Calculate the molar mass of the acid if 25.0 mL of this solution required 11.1 mL of 1.00 M KOH for neutralization. Assume that both protons of the acid are titrated.
- 17.19 Calculate the pH at the equivalence point for these titrations: (a) 0.10 M HCl versus 0.10 M  $\text{NH}_3$ , (b) 0.10 M  $\text{CH}_3\text{COOH}$  versus 0.10 M NaOH.
- 17.20 A sample of 0.1276 g of an unknown monoprotic acid was dissolved in 25.0 mL of water and titrated with 0.0633 M NaOH solution. The volume of base required to reach the equivalence point was 18.4 mL. (a) Calculate the molar mass of the acid. (b) After 10.0 mL of base had been added to the titration, the pH was determined to be 5.87. What is the  $K_a$  of the unknown acid?

### Acid-Base Indicators

#### Review Questions

- 17.21 Explain how an acid-base indicator works in a titration.
- 17.22 What are the criteria for choosing an indicator for a particular acid-base titration?

#### Problems

- 17.23 The amount of indicator used in an acid-base titration must be small. Why?
- 17.24 A student carried out an acid-base titration by adding NaOH solution from a buret to an Erlenmeyer flask containing HCl solution and using phenolphthalein as indicator. At the equivalence point, he observed a faint reddish-pink color. However, after a few minutes, the solution gradually turned colorless. What do you suppose happened?
- 17.25 Referring to Table 17.1, specify which indicator or indicators you would use for the following titrations: (a)  $\text{HCOOH}$  versus NaOH, (b) HCl versus KOH, (c)  $\text{HNO}_3$  versus  $\text{NH}_3$ .

- 17.26** The ionization constant  $K_a$  of an indicator HIn is  $1.0 \times 10^{-6}$ . The color of the nonionized form is red and that of the ionized form is yellow. What is the color of this indicator in a solution whose pH is 4.00? (*Hint:* The color of an indicator can be estimated by considering the ratio  $[HIn]/[In^-]$ . If the ratio is equal to or greater than 10, the color will be that of the nonionized form. If the ratio is equal to or smaller than 0.1, the color will be that of the ionized form.)

## Solubility and Solubility Product

### Review Questions

- 17.27 Define solubility, molar solubility, and solubility product. Explain the difference between solubility and the solubility product of a slightly soluble substance such as BaSO<sub>4</sub>.
- 17.28 Why do we usually not quote the  $K_{sp}$  values for soluble ionic compounds?
- 17.29 Write balanced equations and solubility product expressions for the solubility equilibria of these compounds: (a) CuBr, (b) ZnC<sub>2</sub>O<sub>4</sub>, (c) Ag<sub>2</sub>CrO<sub>4</sub>, (d) Hg<sub>2</sub>Cl<sub>2</sub>, (e) AuCl<sub>3</sub>, (f) Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.
- 17.30 Write the solubility product expression for the ionic compound A<sub>x</sub>B<sub>y</sub>.
- 17.31 How can we predict whether a precipitate will form when two solutions are mixed?
- 17.32 Silver chloride has a larger  $K_{sp}$  than silver carbonate (see Table 17.2). Does this mean that the former also has a larger molar solubility than the latter?

### Problems

- 17.33 Calculate the concentration of ions in these saturated solutions:
- $[I^-]$  in AgI solution with  $[Ag^+] = 9.1 \times 10^{-9} M$
  - $[Al^{3+}]$  in Al(OH)<sub>3</sub> with  $[OH^-] = 2.9 \times 10^{-9} M$
- 17.34** From the solubility data given, calculate the solubility products for these compounds:
- SrF<sub>2</sub>,  $7.3 \times 10^{-2} g/L$
  - Ag<sub>3</sub>PO<sub>4</sub>,  $6.7 \times 10^{-3} g/L$
- 17.35 The molar solubility of MnCO<sub>3</sub> is  $4.2 \times 10^{-6} M$ . What is  $K_{sp}$  for this compound?
- 17.36** Using data from Table 17.2, calculate the molar solubility of calcium phosphate, which is a component of bones.
- 17.37 The solubility of an ionic compound M<sub>2</sub>X<sub>3</sub> (molar mass = 288 g) is  $3.6 \times 10^{-17} g/L$ . What is  $K_{sp}$  for the compound?
- 17.38** Using data from Table 17.2, calculate the solubility of CaF<sub>2</sub> in g/L.
- 17.39 What is the pH of a saturated zinc hydroxide solution?

- 17.40** The pH of a saturated solution of a metal hydroxide MOH is 9.68. Calculate the  $K_{sp}$  for the compound.
- 17.41 A sample of 20.0 mL of 0.10  $M$  Ba(NO<sub>3</sub>)<sub>2</sub> is added to 50.0 mL of 0.10  $M$  Na<sub>2</sub>CO<sub>3</sub>. Will BaCO<sub>3</sub> precipitate?
- 17.42** A volume of 75 mL of 0.060  $M$  NaF is mixed with 25 mL of 0.15  $M$  Sr(NO<sub>3</sub>)<sub>2</sub>. Calculate the concentrations in the final solution of NO<sub>3</sub><sup>-</sup>, Na<sup>+</sup>, Sr<sup>2+</sup>, and F<sup>-</sup>. ( $K_{sp}$  for SrF<sub>2</sub> =  $2.0 \times 10^{-10}$ .)

## The Common Ion Effect

### Review Questions

- 17.43 How does a common ion affect solubility? Use Le Châtelier's principle to explain the decrease in solubility of CaCO<sub>3</sub> in a Na<sub>2</sub>CO<sub>3</sub> solution.
- 17.44 The molar solubility of AgCl in  $6.5 \times 10^{-3} M$  AgNO<sub>3</sub> is  $2.5 \times 10^{-8} M$ . In deriving  $K_{sp}$  from these data, which of these assumptions are reasonable?
- $K_{sp}$  is the same as solubility.
  - $K_{sp}$  of AgCl is the same in  $6.5 \times 10^{-3} M$  AgNO<sub>3</sub> as in pure water.
  - Solubility of AgCl is independent of the concentration of AgNO<sub>3</sub>.
  - [Ag<sup>+</sup>] in solution does not change significantly on the addition of AgCl to  $6.5 \times 10^{-3} M$  AgNO<sub>3</sub>.
  - [Ag<sup>+</sup>] in solution after the addition of AgCl to  $6.5 \times 10^{-3} M$  AgNO<sub>3</sub> is the same as it would be in pure water.

### Problems

- 17.45 How many grams of CaCO<sub>3</sub> will dissolve in 3.0  $\times$  10<sup>2</sup> mL of 0.050  $M$  Ca(NO<sub>3</sub>)<sub>2</sub>?
- 17.46** The solubility product of PbBr<sub>2</sub> is  $8.9 \times 10^{-6}$ . Determine the molar solubility (a) in pure water, (b) in 0.20  $M$  KBr solution, (c) in 0.20  $M$  Pb(NO<sub>3</sub>)<sub>2</sub> solution.
- 17.47 Calculate the molar solubility of AgCl in a solution made by dissolving 10.0 g of CaCl<sub>2</sub> in 1.00 L of solution.
- 17.48** Calculate the molar solubility of BaSO<sub>4</sub> (a) in water and (b) in a solution containing 1.0  $M$  SO<sub>4</sub><sup>2-</sup> ions.

## Complex Ions

### Review Questions

- 17.49 Explain the formation of complexes in Table 17.4 in terms of Lewis acid-base theory.
- 17.50 Give an example to illustrate the general effect of complex ion formation on solubility.

### Problems

- 17.51 Write the formation constant expressions for these complex ions: (a) Zn(OH)<sub>4</sub><sup>2-</sup>, (b) Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, (c) HgI<sub>4</sub><sup>2-</sup>.

- 17.52** Explain, with balanced ionic equations, why (a)  $\text{CuI}_2$  dissolves in ammonia solution, (b)  $\text{AgBr}$  dissolves in  $\text{NaCN}$  solution, (c)  $\text{Hg}_2\text{Cl}_2$  dissolves in  $\text{KCl}$  solution.
- 17.53 If 2.50 g of  $\text{CuSO}_4$  are dissolved in  $9.0 \times 10^2$  mL of 0.30 M  $\text{NH}_3$ , what are the concentrations of  $\text{Cu}^{2+}$ ,  $\text{Cu}(\text{NH}_3)_4^{2+}$ , and  $\text{NH}_3$  at equilibrium?
- 17.54** Calculate the concentrations of  $\text{Cd}^{2+}$ ,  $\text{Cd}(\text{CN})_4^{2-}$ , and  $\text{CN}^-$  at equilibrium when 0.50 g of  $\text{Cd}(\text{NO}_3)_2$  dissolves in  $5.0 \times 10^2$  mL of 0.50 M  $\text{NaCN}$ .
- 17.55 If  $\text{NaOH}$  is added to 0.010 M  $\text{Al}^{3+}$ , which will be the predominant species at equilibrium:  $\text{Al}(\text{OH})_3$  or  $\text{Al}(\text{OH})_4^-$ ? The pH of the solution is 14.00. [ $K_f$  for  $\text{Al}(\text{OH})_4^- = 2.0 \times 10^{33}$ .]
- 17.56** Calculate the molar solubility of  $\text{AgI}$  in a 1.0 M  $\text{NH}_3$  solution. (*Hint:* You need to consider two different types of equilibria.)

## Qualitative Analysis

### Review Questions

- 17.57 Outline the general principle of qualitative analysis.
- 17.58 Give two examples of metal ions in each group (1 through 5) in the qualitative analysis scheme.

### Problems

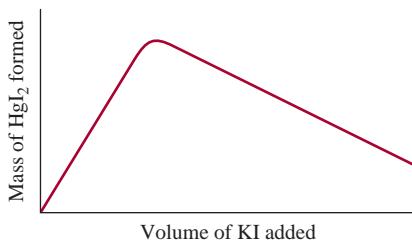
- 17.59 In a group 1 analysis, a student obtained a precipitate containing both  $\text{AgCl}$  and  $\text{PbCl}_2$ . Suggest one reagent that would allow her to separate  $\text{AgCl}(s)$  from  $\text{PbCl}_2(s)$ .
- 17.60** In a group 1 analysis, a student adds hydrochloric acid to the unknown solution to make  $[\text{Cl}^-] = 0.15$  M. Some  $\text{PbCl}_2$  precipitates. Calculate the concentration of  $\text{Pb}^{2+}$  remaining in solution.
- 17.61 Both  $\text{KCl}$  and  $\text{NH}_4\text{Cl}$  are white solids. Suggest one reagent that would enable you to distinguish between these two compounds.
- 17.62** Describe a simple test that would enable you to distinguish between  $\text{AgNO}_3(s)$  and  $\text{Cu}(\text{NO}_3)_2(s)$ .

## Additional Problems

- 17.63 A quantity of 0.560 g of  $\text{KOH}$  is added to 25.0 mL of 1.00 M  $\text{HCl}$ . Excess  $\text{Na}_2\text{CO}_3$  is then added to the solution. What mass (in grams) of  $\text{CO}_2$  is formed?
- 17.64** A volume of 25.0 mL of 0.100 M  $\text{HCl}$  is titrated against a 0.100 M  $\text{NH}_3$  solution added to it from a buret. Calculate the pH values of the solution (a) after 10.0 mL of  $\text{NH}_3$  solution have been added, (b) after 25.0 mL of  $\text{NH}_3$  solution have been added, (c) after 35.0 mL of  $\text{NH}_3$  solution have been added.
- 17.65 The buffer range is defined by the equation  $\text{pH} = \text{p}K_a \pm 1$ . Calculate the range of the ratio [conjugate base]/[acid] that corresponds to this equation.

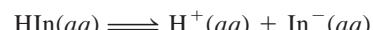
- 17.66** The  $\text{p}K_a$  of the indicator methyl orange is 3.46. Over what pH range does this indicator change from 90%  $\text{HIn}$  to 90%  $\text{In}^-$ ?
- 17.67 Sketch the titration curve of a weak acid versus a strong base such as that shown in Figure 17.5. On your graph indicate the volume of base used at the equivalence point and also at the half-equivalence point, that is, the point at which half of the base has been added. Show how you can measure the pH of the solution at the half-equivalence point. Using Equation (17.3), explain how you can determine the  $\text{p}K_a$  of the acid by this procedure.
- 17.68** A 200-mL volume of  $\text{NaOH}$  solution was added to 400 mL of a 2.00 M  $\text{HNO}_2$  solution. The pH of the mixed solution was 1.50 units greater than that of the original acid solution. Calculate the molarity of the  $\text{NaOH}$  solution.
- 17.69 The  $\text{p}K_a$  of butyric acid ( $\text{HBut}$ ) is 4.7. Calculate  $K_b$  for the butyrate ion ( $\text{But}^-$ ).
- 17.70** A solution is made by mixing exactly 500 mL of 0.167 M  $\text{NaOH}$  with exactly 500 mL 0.100 M  $\text{CH}_3\text{COOH}$ . Calculate the equilibrium concentrations of  $\text{H}^+$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{OH}^-$ , and  $\text{Na}^+$ .
- 17.71  $\text{Cd(OH)}_2$  is an insoluble compound. It dissolves in a  $\text{NaOH}$  solution. Write a balanced ionic equation for this reaction. What type of reaction is this?
- 17.72** Calculate the pH of the 0.20 M  $\text{NH}_3$ /0.20 M  $\text{NH}_4\text{Cl}$  buffer. What is the pH of the buffer after the addition of 10.0 mL of 0.10 M  $\text{HCl}$  to 65.0 mL of the buffer?
- 17.73 For which of these reactions is the equilibrium constant called a solubility product?
- $\text{Zn}(\text{OH})_2(s) + 2\text{OH}^-(aq) \rightleftharpoons \text{Zn}(\text{OH})_4^{2-}(aq)$
  - $3\text{Ca}^{2+}(aq) + 2\text{PO}_4^{3-}(aq) \rightleftharpoons \text{Ca}_3(\text{PO}_4)_2(s)$
  - $\text{CaCO}_3(s) + 2\text{H}^+(aq) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$
  - $\text{PbI}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{I}^-(aq)$
- 17.74** A student mixes 50.0 mL of 1.00 M  $\text{Ba}(\text{OH})_2$  with 86.4 mL of 0.494 M  $\text{H}_2\text{SO}_4$ . Calculate the mass of  $\text{BaSO}_4$  formed and the pH of the mixed solution.
- 17.75 A 2.0-L kettle contains 116 g of calcium carbonate as boiler scale. How many times would the kettle have to be completely filled with distilled water to remove all of the deposit at 25°C?
- 17.76** Equal volumes of 0.12 M  $\text{AgNO}_3$  and 0.14 M  $\text{ZnCl}_2$  solution are mixed. Calculate the equilibrium concentrations of  $\text{Ag}^+$ ,  $\text{Cl}^-$ ,  $\text{Zn}^{2+}$ , and  $\text{NO}_3^-$ .
- 17.77 Calculate the solubility (in grams per liter) of  $\text{Ag}_2\text{CO}_3$ .
- 17.78** Find the approximate pH range suitable for the separation of  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$  by precipitation of  $\text{Fe}(\text{OH})_3$  from a solution that is initially 0.010 M in  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$ .

- 17.79 Which of these ionic compounds will be more soluble in acid solution than in water: (a)  $\text{BaSO}_4$ , (b)  $\text{PbCl}_2$ , (c)  $\text{Fe(OH)}_3$ , (d)  $\text{CaCO}_3$ ? Explain. (*Hint:* For each salt, determine any possible reaction between the anion and  $\text{H}^+$  ions.)
- 17.80 Which of these substances will be more soluble in acid solution than in pure water: (a)  $\text{CuI}$ , (b)  $\text{Ag}_2\text{SO}_4$ , (c)  $\text{Zn}(\text{OH})_2$ , (d)  $\text{BaC}_2\text{O}_4$ , (e)  $\text{Ca}_3(\text{PO}_4)_2$ ? Explain. (*Hint:* For each salt, determine any possible reaction between the anion and  $\text{H}^+$  ions.)
- 17.81 What is the pH of a saturated solution of aluminum hydroxide?
- 17.82 The molar solubility of  $\text{Pb}(\text{IO}_3)_2$  in a  $0.10\text{ M}$   $\text{NaIO}_3$  solution is  $2.4 \times 10^{-11}\text{ mol/L}$ . What is  $K_{\text{sp}}$  for  $\text{Pb}(\text{IO}_3)_2$ ?
- 17.83 The solubility product of  $\text{Mg}(\text{OH})_2$  is  $1.2 \times 10^{-11}$ . What minimum  $\text{OH}^-$  concentration must be attained (for example, by adding  $\text{NaOH}$ ) to make the  $\text{Mg}^{2+}$  concentration in a solution of  $\text{Mg}(\text{NO}_3)_2$  less than  $1.0 \times 10^{-10}\text{ M}$ ?
- 17.84 Calculate whether a precipitate will form if  $2.00\text{ mL}$  of  $0.60\text{ M}$   $\text{NH}_3$  are added to  $1.0\text{ L}$  of  $1.0 \times 10^{-3}\text{ M}$   $\text{FeSO}_4$ .
- 17.85 Both  $\text{Ag}^+$  and  $\text{Zn}^{2+}$  form complex ions with  $\text{NH}_3$ . Write balanced equations for the reactions. However,  $\text{Zn}(\text{OH})_2$  is soluble in  $6\text{ M}$   $\text{NaOH}$ , and  $\text{AgOH}$  is not. Explain.
- 17.86 When a KI solution was added to a solution of mercury(II) chloride, a precipitate [mercury(II) iodide] was formed. A student plotted the mass of the precipitate formed versus the volume of the KI solution added and obtained the graph shown here. Explain the appearance of the graph.



- 17.87 Barium is a toxic substance that can cause serious deterioration of the heart's function. In a barium enema procedure, a patient drinks an aqueous suspension of  $20\text{ g}$   $\text{BaSO}_4$ . If this substance were to equilibrate with the  $5.0\text{ L}$  of the blood in the patient's body, how many grams of  $\text{BaSO}_4$  will dissolve in the blood? For a good estimate, we may assume that the temperature is  $25^\circ\text{C}$ . Why is  $\text{Ba}(\text{NO}_3)_2$  not chosen for this procedure?
- 17.88 The  $pK_a$  of phenolphthalein is 9.10. Over what pH range does this indicator change from 95%  $\text{HIn}$  to 95%  $\text{In}^-$ ?
- 17.89 Look up the  $K_{\text{sp}}$  values for  $\text{BaSO}_4$  and  $\text{SrSO}_4$  in Table 17.2. Calculate  $[\text{Ba}^{2+}]$ ,  $[\text{Sr}^{2+}]$ , and  $[\text{SO}_4^{2-}]$  in a solution that is saturated with both compounds.
- 17.90 Solid  $\text{NaI}$  is slowly added to a solution that is  $0.010\text{ M}$  in  $\text{Cu}^+$  and  $0.010\text{ M}$  in  $\text{Ag}^+$ . (a) Which compound will begin to precipitate first? (b) Calculate  $[\text{Ag}^+]$  when  $\text{CuI}$  just begins to precipitate. (c) What percentage of  $\text{Ag}^+$  remains in solution at this point?
- 17.91 Radiochemical techniques are useful in estimating the solubility product of many compounds. In one experiment,  $50.0\text{ mL}$  of a  $0.010\text{ M}$   $\text{AgNO}_3$  solution containing a silver isotope with a radioactivity of 74,025 counts per min per mL were mixed with  $100\text{ mL}$  of a  $0.030\text{ M}$   $\text{NaIO}_3$  solution. The mixed solution was diluted to  $500\text{ mL}$  and filtered to remove all of the  $\text{AgIO}_3$  precipitate. The remaining solution was found to have a radioactivity of 44.4 counts per min per mL. What is the  $K_{\text{sp}}$  of  $\text{AgIO}_3$ ?
- 17.92 The molar mass of a certain metal carbonate,  $\text{MCO}_3$ , can be determined by adding an excess of HCl acid to react with the carbonate and then "back-titration" the remaining acid with NaOH. (a) Write an equation for these reactions. (b) In a certain experiment,  $20.00\text{ mL}$  of  $0.0800\text{ M}$  HCl were added to a  $0.1022\text{-g}$  sample of  $\text{MCO}_3$ . The excess HCl required  $5.64\text{ mL}$  of  $0.1000\text{ M}$  NaOH for neutralization. Calculate the molar mass of the carbonate and identify M.
- 17.93 Acid-base reactions usually go to completion. Confirm this statement by calculating the equilibrium constant for each of the following cases: (a) a strong acid reacting with a strong base, (b) a strong acid reacting with a weak base ( $\text{NH}_3$ ), (c) a weak acid ( $\text{CH}_3\text{COOH}$ ) reacting with a strong base, (d) a weak acid ( $\text{CH}_3\text{COOH}$ ) reacting with a weak base ( $\text{NH}_3$ ). (*Hint:* Strong acids exist as  $\text{H}^+$  ions and strong bases exist as  $\text{OH}^-$  ions in solution. You need to look up the  $K_a$ ,  $K_b$ , and  $K_w$  values.)
- 17.94 Calculate  $x$ , the number of molecules of water in oxalic acid hydrate,  $\text{H}_2\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ , from the following data:  $5.00\text{ g}$  of the compound is made up to exactly  $250\text{ mL}$  solution and  $25.0\text{ mL}$  of this solution requires  $15.9\text{ mL}$  of  $0.500\text{ M}$   $\text{NaOH}$  solution for neutralization.
- 17.95 Describe how you would prepare  $1\text{ L}$  of the buffer  $0.20\text{ M}$   $\text{CH}_3\text{COONa}/0.20\text{ M}$   $\text{CH}_3\text{COOH}$  by (a) mixing a solution of  $\text{CH}_3\text{COOH}$  with a solution of  $\text{CH}_3\text{COONa}$ , (b) reacting a solution of  $\text{CH}_3\text{COOH}$  with a solution of  $\text{NaOH}$ , and (c) reacting a solution of  $\text{CH}_3\text{COONa}$  with a solution of  $\text{HCl}$ .
- 17.96 What reagents would you employ to separate these pairs of ions in solution: (a)  $\text{Na}^+$  and  $\text{Ba}^{2+}$ , (b)  $\text{K}^+$  and  $\text{Pb}^{2+}$ , (c)  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$ ?

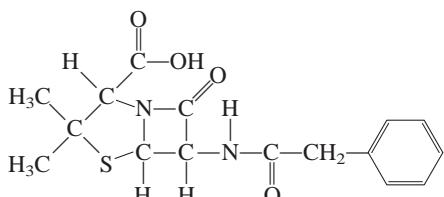
- 17.97  $\text{CaSO}_4$  ( $K_{\text{sp}} = 2.4 \times 10^{-5}$ ) has a larger  $K_{\text{sp}}$  value than that of  $\text{Ag}_2\text{SO}_4$  ( $K_{\text{sp}} = 1.4 \times 10^{-5}$ ). Does it follow that  $\text{CaSO}_4$  also has greater solubility (g/L)?
- 17.98 How many milliliters of 1.0 M NaOH must be added to 200 mL of 0.10 M  $\text{NaH}_2\text{PO}_4$  to make a buffer solution with a pH of 7.50?
- 17.99 The maximum allowable concentration of  $\text{Pb}^{2+}$  ions in drinking water is 0.05 ppm (that is, 0.05 g of  $\text{Pb}^{2+}$  in 1 million g of water). Is this guideline exceeded if an underground water supply is at equilibrium with the mineral anglesite,  $\text{PbSO}_4$  ( $K_{\text{sp}} = 1.6 \times 10^{-8}$ )?
- 17.100 Which of these solutions has the highest  $[\text{H}^+]$ : (a) 0.10 M HF, (b) 0.10 M HF in 0.10 M NaF, or (c) 0.10 M HF in 0.10 M  $\text{SbF}_5^-$ ? (Hint:  $\text{SbF}_5^-$  reacts with  $\text{F}^-$  to form the complex ion  $\text{SbF}_6^-$ .)
- 17.101 Distribution curves show how the fractions of non-ionized acid and its conjugate base vary as a function of pH of the medium. Plot distribution curves for  $\text{CH}_3\text{COOH}$  and its conjugate base  $\text{CH}_3\text{COO}^-$  in solution. Your graph should show fraction as the y axis and pH as the x axis. What are the fractions and pH at the point these two curves intersect?
- 17.102 Water containing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions is called *hard water* and is unsuitable for some household and industrial use because these ions react with soap to form insoluble salts, or curds. One way to remove the  $\text{Ca}^{2+}$  ions from hard water is by adding washing
- soda ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ). (a) The molar solubility of  $\text{CaCO}_3$  is  $9.3 \times 10^{-5}$  M. What is its molar solubility in a 0.050 M  $\text{Na}_2\text{CO}_3$  solution? (b) Why are  $\text{Mg}^{2+}$  ions not removed by this procedure? (c) The  $\text{Mg}^{2+}$  ions are removed as  $\text{Mg}(\text{OH})_2$  by adding slaked lime [ $\text{Ca}(\text{OH})_2$ ] to the water to produce a saturated solution. Calculate the pH of a saturated  $\text{Ca}(\text{OH})_2$  solution. (d) What is the concentration of  $\text{Mg}^{2+}$  ions at this pH? (e) In general, which ion ( $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ ) would you remove first? Why?
- 17.103 (a) Referring to Figure 17.6, describe how you would determine the  $pK_b$  of the base. (b) Derive an analogous Henderson-Hasselbalch equation relating  $\text{pOH}$  to  $pK_b$  of a weak base B and its conjugate acid  $\text{HB}^+$ . Sketch a titration curve showing the variation of the  $\text{pOH}$  of the base solution versus the volume of a strong acid added from a buret. Describe how you would determine the  $pK_b$  from this curve.
- 17.104 Consider the ionization of the following acid-base indicator:



The indicator changes color according to the ratios of the concentrations of the acid to its conjugate base as described on p. 587. Show that the pH range over which the indicator changes from the acid color to the base color is  $\text{pH} = pK_a \pm 1$ , where  $K_a$  is the ionization constant of the acid.

## SPECIAL PROBLEMS

- 17.105 One of the most commonly used antibiotics is penicillin G (benzylpenicillanic acid), which has the following structure:



It is a weak monoprotic acid:



in which HP denotes the parent acid and  $\text{P}^-$  the conjugate base. Penicillin G is produced by growing molds in fermentation tanks at 25°C and a pH range of 4.5 to 5.0. The crude form of this antibiotic is obtained by extracting the fermentation broth with an organic solvent in which the acid is soluble. (a) Identify the acidic hydrogen atom. (b) In one stage of purification, the organic extract of the crude penicillin G is treated

with a buffer solution at pH = 6.50. What is the ratio of the conjugate base of penicillin G to the acid at this pH? Would you expect the conjugate base to be more soluble in water than the acid? (c) Penicillin G is not suitable for oral administration, but the sodium salt (NaP) is because it is soluble. Calculate the pH of a 0.12 M NaP solution formed when a tablet containing the salt is dissolved in a glass of water.

- 17.106 Amino acids are the building blocks of proteins. These compounds contain at least one amino group and one carboxyl group. Consider glycine, whose structure is shown in Figure 11.18. Depending on the pH of the solution, glycine can exist in one of three possible forms:

Fully protonated:  $\text{NH}_3^+—\text{CH}_2—\text{COOH}$

Dipolar ion:  $\text{NH}_3^+—\text{CH}_2—\text{COO}^-$

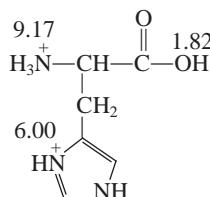
Fully ionized:  $\text{NH}_2—\text{CH}_2—\text{COO}^-$

Predict the predominant form of glycine at pH 1.0, 7.0, and 12.0. The  $pK_a$  of the carboxyl group is 2.3 and that of the ammonium group is 9.6. [Hint: Use Equation (17.3).]

**17.107** One way to distinguish a buffer solution with an acid solution is by dilution. (a) Consider a buffer solution made of 0.500 M CH<sub>3</sub>COOH and 0.500 M CH<sub>3</sub>COONa. Calculate its pH and the pH after it has been diluted 10-fold. (b) Compare the result in (a) with the pHs of a 0.500 M CH<sub>3</sub>COOH solution before and after it has been diluted 10-fold.

**17.108** A sample of 0.96 L of HCl at 372 mmHg and 22°C is bubbled into 0.034 L of 0.57 M NH<sub>3</sub>. What is the pH of the resulting solution? Assume the volume of solution remains constant and that the HCl is totally dissolved in the solution.

**17.109** Histidine is one of the 20 amino acids found in proteins. Shown here is a fully protonated histidine molecule where the numbers denote the pK<sub>a</sub> values of the acidic groups.



(a) Show stepwise ionization of histidine in solution (*Hint:* The H<sup>+</sup> ion will first come off from the strongest acid group followed by the next strongest acid group and so on.) (b) A dipolar ion is one in which the species has an equal number of positive and negative charges. Identify the dipolar ion in (a). (c) The pH at which the dipolar ion predominates is called the isoelectric point, denoted by *pI*. The isoelectric point is the average of the pK<sub>a</sub> values leading to and following the formation of the dipolar ion. Calculate the *pI* of histidine. (d) The histidine group plays an important role in buffering blood. Which conjugate acid-base pair shown in (a) is responsible for this action?

**17.110** A 1.0-L saturated silver carbonate solution at 5°C is treated with enough hydrochloric acid to decompose the compound. The carbon dioxide generated is collected in a 19-mL vial and exerts a pressure of 114 mmHg at 25°C. What is the K<sub>sp</sub> of Ag<sub>2</sub>CO<sub>3</sub> at 5°C?

## ANSWERS TO PRACTICE EXERCISES

**17.1** (a) and (c). **17.2** 9.17, 9.20. **17.3** Weigh out Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> in a mole ratio of 0.60 to 1.0. Dissolve in enough water to make up a 1-L solution. **17.4** (a) 2.19, (b) 3.95, (c) 8.02, (d) 11.39. **17.5** (a) Bromophenol blue, methyl orange, methyl red, and chlorophenol blue; (b) all

except thymol blue, bromophenol blue, and methyl orange; (c) cresol red and phenolphthalein. **17.6** 2.0 × 10<sup>-14</sup>.

**17.7** 1.9 × 10<sup>-3</sup> g/L. **17.8** No. **17.9** (a) 1.7 × 10<sup>-4</sup> g/L, (b) 1.4 × 10<sup>-7</sup> g/L. **17.10** [Cu<sup>2+</sup>] = 1.2 × 10<sup>-13</sup> M, [Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>] = 0.017 M, [NH<sub>3</sub>] = 0.23 M.

# 18



The production of quicklime ( $\text{CaO}$ ) from limestone ( $\text{CaCO}_3$ ) in a rotary kiln at about  $950^\circ\text{C}$ .

## Thermodynamics

### CHAPTER OUTLINE

- 18.1** The Three Laws of Thermodynamics 611
- 18.2** Spontaneous Processes 611
- 18.3** Entropy 612
  - Microstates and Entropy • Changes in Entropy • Standard Entropy
- 18.4** The Second Law of Thermodynamics 617
  - Entropy Changes in the System • Entropy Changes in the Surroundings • The Third Law of Thermodynamics and Absolute Entropy
- 18.5** Gibbs Free Energy 622
  - Standard Free-Energy Change • Applications of Equation (18.10)
- 18.6** Free Energy and Chemical Equilibrium 629
- 18.7** Thermodynamics in Living Systems 632

### ESSENTIAL CONCEPTS

**Laws of Thermodynamics** The laws of thermodynamics have been successfully applied to the study of chemical and physical processes. The first law of thermodynamics is based on the law of conservation of energy. The second law of thermodynamics deals with natural or spontaneous processes. The function that predicts the spontaneity of a reaction is entropy. The second law states that for a spontaneous process, the change in the entropy of the universe must be positive. The third law enables us to determine absolute entropy values.

**Gibbs Free Energy** Gibbs free energy helps us to determine the spontaneity of a reaction by focusing only on the system. The change in Gibbs free energy for a process is made up of two terms: a change in enthalpy and a change in entropy times temperature. At constant temperature and pressure, a decrease in Gibbs free energy signals a spontaneous reaction. The change in the standard Gibbs free energy can be related to the equilibrium constant of a reaction.

**Thermodynamics in Living Systems** Many reactions of biological importance are nonspontaneous. By coupling such reactions to those that have a negative Gibbs free energy change with the aid of enzymes, the net reaction can be made to proceed to yield the desired products.



### Activity Summary

1. Interactivity: Entropies of Reactions (18.4)
2. Interactivity: Entropy vs. Temperature (18.4)
3. Interactivity: Free Energy—Equilibrium (18.6)

## 18.1 The Three Laws of Thermodynamics

In Chapter 6 we encountered the first of three laws of thermodynamics, which says that energy can be converted from one form to another, but it cannot be created or destroyed. One measure of these changes is the amount of heat given off or absorbed by a system during a constant-pressure process, which chemists define as a change in enthalpy ( $\Delta H$ ).

The second law of thermodynamics explains why chemical processes tend to favor one direction. The third law is an extension of the second law and will be examined briefly in Section 18.4.

## 18.2 Spontaneous Processes

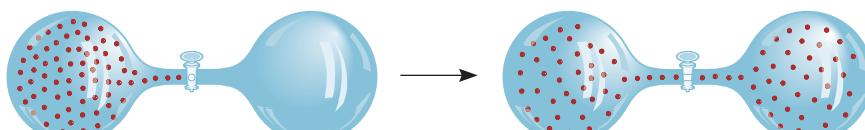
One of the main objectives in studying thermodynamics, as far as chemists are concerned, is to be able to predict whether or not a reaction will occur when reactants are brought together under a specific set of conditions (for example, at a certain temperature, pressure, and concentration). This knowledge is important whether one is synthesizing compounds in a research laboratory, manufacturing chemicals on an industrial scale, or trying to understand the intricate biological processes in a cell. A reaction that *does* occur under the given set of conditions is called a *spontaneous reaction*. If a reaction does not occur under specified conditions, it is said to be non-spontaneous. We observe spontaneous physical and chemical processes every day, including many of the following examples:

- A waterfall runs downhill, but never up, spontaneously.
- A lump of sugar spontaneously dissolves in a cup of coffee, but dissolved sugar does not spontaneously reappear in its original form.
- Water freezes spontaneously below  $0^\circ\text{C}$ , and ice melts spontaneously above  $0^\circ\text{C}$  (at 1 atm).
- Heat flows from a hotter object to a colder one, but the reverse never happens spontaneously.
- The expansion of a gas into an evacuated bulb is a spontaneous process [Figure 18.1(a)]. The reverse process, that is, the gathering of all the molecules into one bulb, is not spontaneous [Figure 18.1(b)].

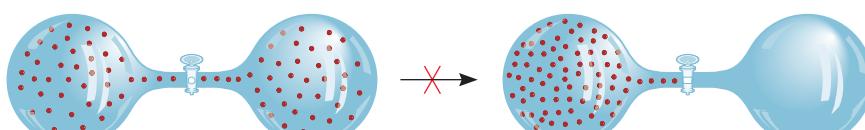
A spontaneous reaction does not necessarily mean an instantaneous reaction.



A spontaneous and a nonspontaneous process.  
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(a)



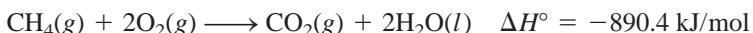
(b)

**Figure 18.1**  
(a) A spontaneous process.  
(b) A nonspontaneous process.

- A piece of sodium metal reacts violently with water to form sodium hydroxide and hydrogen gas. However, hydrogen gas does not react with sodium hydroxide to form water and sodium.
- Iron exposed to water and oxygen forms rust, but rust does not spontaneously change back to iron.

These examples show that processes that occur spontaneously in one direction cannot, under the same conditions, also take place spontaneously in the opposite direction.

If we assume that spontaneous processes occur so as to decrease the energy of a system, we can explain why a ball rolls downhill and why springs in a clock unwind. Similarly, a large number of exothermic reactions are spontaneous. An example is the combustion of methane:



Another example is the acid-base neutralization reaction:



But consider a solid-to-liquid phase transition such as

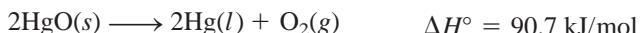


In this case, the assumption that spontaneous processes always decrease a system's energy fails. Experience tells us that ice melts spontaneously above 0°C even though the process is endothermic. Another example that contradicts our assumption is the dissolution of ammonium nitrate in water:



When heated,  $\text{HgO}$  decomposes to give  $\text{Hg}$  and  $\text{O}_2$ .

This process is spontaneous, and yet it is also endothermic. The decomposition of mercury(II) oxide is an endothermic reaction that is nonspontaneous at room temperature, but it becomes spontaneous when the temperature is raised:



From a study of the examples mentioned and many more cases, we come to the following conclusion: Exothermicity favors the spontaneity of a reaction but does not guarantee it. Just as it is possible for an endothermic reaction to be spontaneous, it is possible for an exothermic reaction to be nonspontaneous. In other words, we cannot decide whether or not a chemical reaction will occur spontaneously solely on the basis of energy changes in the system. To make this kind of prediction we need another thermodynamic quantity, which turns out to be *entropy*.

### 18.3 Entropy

In order to predict the spontaneity of a process, we need to introduce a new thermodynamic quantity called entropy. **Entropy ( $S$ )** is often described as *a measure of how spread out or dispersed the energy of a system is among the different possible ways that system can contain energy*. The greater the dispersal, the greater is the entropy. Most processes are accompanied by a change in entropy. A cup of hot water has a certain amount of entropy due to the dispersal of energy among the various energy states of the water molecules (for example, energy states associated with the

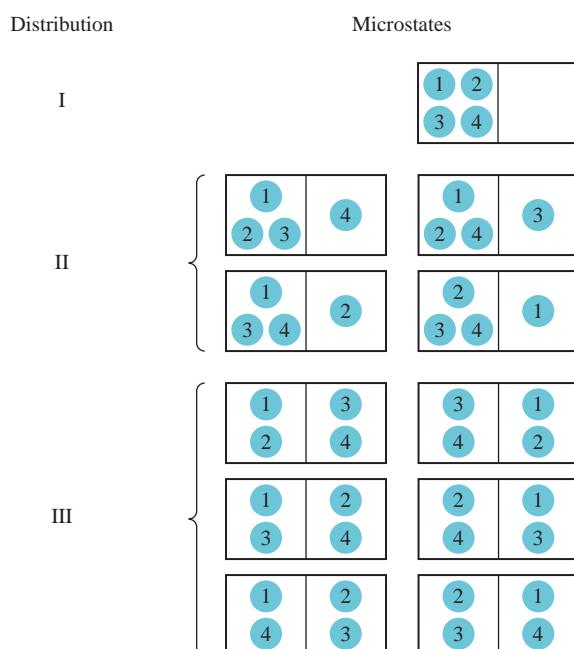
translational, rotational, and vibrational motions of the water molecules). If left standing on a table, the water loses heat to the cooler surroundings. Consequently, there is an increase in entropy because of the dispersal of energy over a great many energy states of the air molecules.

**Translational motion is motion through space of the whole molecule.**

As another example, consider the situation depicted in Figure 18.1. Before the valve is opened, the system possesses a certain amount of entropy. Upon opening the valve, the gas molecules now have access to the combined volume of both bulbs. A larger volume for movement results in a narrowing of the gap between translational energy levels of the molecules. Consequently, the entropy of the system increases because closely spaced energy levels leads to a greater dispersal among the energy levels.

## Micromolecules and Entropy

Before we introduce the second law of thermodynamics, which relates entropy change (increase) to spontaneous processes, it is useful to first provide a proper definition of entropy. To do so let us consider a simple system of four molecules distributed between two equal compartments, as shown in Figure 18.2. There is only one way to arrange all the molecules in the left compartment, four ways to have three molecules in the left compartment and one in the right compartment, and six ways to have two molecules in each of the two compartments. The eleven possible ways of distributing the molecules are called microscopic states or microstates and each set of similar microstates is called a distribution.<sup>†</sup> As you can see, distribution III is the most probable because there are six microstates or six ways to achieve it and distribution I is the least probable because it has one microstate and therefore there is only one way to achieve it. Based on this analysis, we conclude that the probability of occurrence

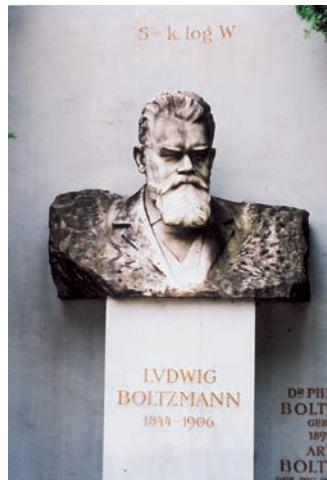


**Figure 18.2**

*Some possible ways of distributing four molecules between two equal compartments. Distribution I can be achieved in only one way (all four molecules in the left compartment) and has one microstate. Distribution II can be achieved in four ways and has four microstates. Distribution III can be achieved in six ways and has six microstates.*

<sup>†</sup>Actually there are still other possible ways to distribute the four molecules between the two compartments. We can have all four molecules in the right compartment (one way) and three molecules in the right compartment and one molecule in the left compartment (four ways). However, the distributions shown in Figure 18.2 are sufficient for our discussion.

of a particular distribution (state) depends on the number of ways (microstates) in which the distribution can be achieved. As the number of molecules approaches macroscopic scale, it is not difficult to see that they will be evenly distributed between the two compartments because this distribution has many, many more microstates than all other distributions.



Engraved on Ludwig Boltzmann's tombstone in Vienna is his famous equation. The "log" stands for "log<sub>e</sub>," which is the natural logarithm or ln.

In 1868 Boltzmann showed that the entropy of a system is related to the natural log of the number of microstates ( $W$ ):

$$S = k \ln W \quad (18.1)$$

where  $k$  is called the Boltzmann constant ( $1.38 \times 10^{-23}$  J/K). Thus, the larger the  $W$ , the greater is the entropy of the system. Like enthalpy, entropy is a state function (see Section 6.3). Consider a certain process in a system. The entropy change for the process,  $\Delta S$ , is

$$\Delta S = S_f - S_i \quad (18.2)$$

where  $S_i$  and  $S_f$  are the entropies of the system in the initial and final states, respectively. From Equation (18.1) we can write

$$\begin{aligned} \Delta S &= k \ln W_f - k \ln W_i \\ &= k \ln \frac{W_f}{W_i} \end{aligned} \quad (18.3)$$

where  $W_i$  and  $W_f$  are the corresponding numbers of microstates in the initial and final state. Thus, if  $W_f > W_i$ ,  $\Delta S > 0$  and the entropy of the system increases.

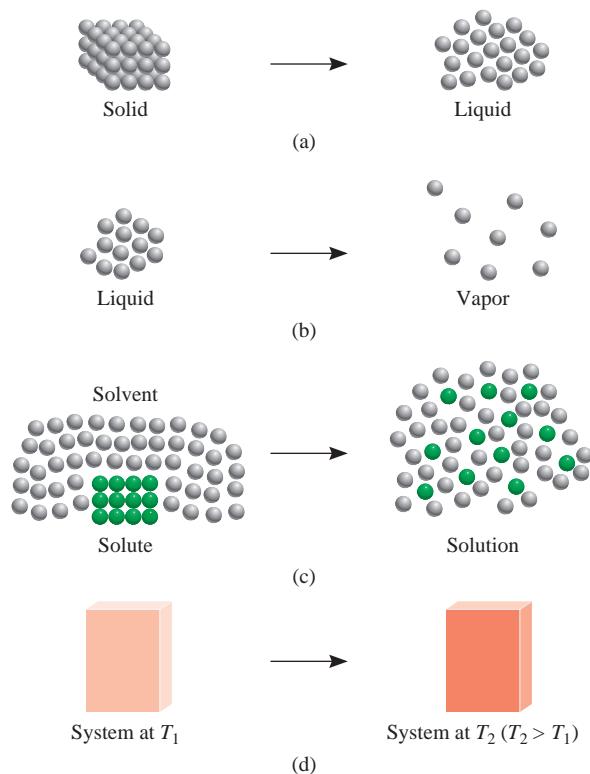
## Changes in Entropy

Earlier we described the increase in entropy of a system as a result of the increase in the dispersal of energy. There is a connection between the qualitative description of entropy in terms of dispersal of energy and the quantitative definition of entropy in terms of microstates given by Equation (18.1). We conclude that

- A system with fewer microstates (smaller  $W$ ) among which to spread its energy (small dispersal) has a lower entropy.
- A system with more microstates (larger  $W$ ) among which to spread its energy (large dispersal) has a higher entropy.

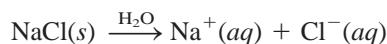
Next, we will study several processes that lead to a change in entropy of a system in terms of the change in the number of microstates of the system.

Consider the situations shown in Figure 18.3. In a solid the atoms or molecules are confined to fixed positions and the number of microstates is small. Upon melting, these atoms or molecules can occupy many more positions as they move away from the lattice points. Consequently, the number of microstates increases because there are now many more ways to arrange the particles. Therefore, we predict this "order → disorder" phase transition to result in an increase in entropy because the number of microstates has increased. Similarly, we predict the vaporization process will also lead to an increase in the entropy of the system. The increase will be considerably greater than that for melting, however, because molecules in the gas phase occupy much more space, and therefore there are far more microstates than in the liquid phase. The solution process usually leads to an increase in entropy. When a sugar crystal dissolves in water, the highly ordered structure of the solid and part of



**Figure 18.3**  
Processes that lead to an increase in entropy of the system: (a) melting:  $S_{\text{liquid}} > S_{\text{solid}}$ ; (b) vaporization:  $S_{\text{vapor}} > S_{\text{liquid}}$ ; (c) dissolving; (d) heating:  $S_{T_2} > S_{T_1}$ .

the ordered structure of water break down. Thus, the solution has a greater number of microstates than the pure solute and pure solvent combined. When an ionic solid such as NaCl dissolves in water, there are two contributions to entropy increase: the solution process (mixing of solute with solvent) and the dissociation of the compound into ions:



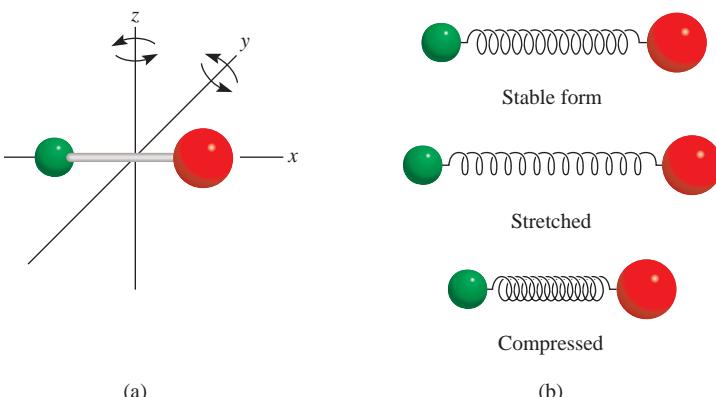
More particles lead to a greater number of microstates. However, we must also consider hydration, which causes water molecules to become more ordered around the ions. This process decreases entropy because it reduces the number of microstates of the solvent molecules. For small, highly charged ions such as  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ , the decrease in entropy due to hydration can outweigh the increase in entropy due to mixing and dissociation so that the entropy change for the overall process can actually be negative. Heating also increases the entropy of a system. In addition to translational motion, molecules can also execute rotational motions and vibrational motions (Figure 18.4). As the temperature is increased, the energies associated with all types of molecular motion increase. This increase in energy is distributed or dispersed among the quantized energy levels. Consequently, more microstates become available at a higher temperature; therefore, the entropy of a system always increases with increasing temperature.

## Standard Entropy

Equation (18.1) provides a useful molecular interpretation of entropy, but is normally not used to calculate the entropy of a system because it is difficult to determine the

**Figure 18.4**

(a) A diatomic molecule can rotate about the  $y$ - and  $z$ -axes (the  $x$ -axis is along the bond).  
 (b) Vibrational motion of a diatomic molecule. Chemical bonds can be stretched and compressed like a spring.

**TABLE 18.1**
**Standard Entropy Values ( $S^\circ$ ) for Some Substances at 25°C**

| Substance                       | $S^\circ$<br>(J/K · mol) |
|---------------------------------|--------------------------|
| $\text{H}_2\text{O}(l)$         | 69.9                     |
| $\text{H}_2\text{O}(g)$         | 188.7                    |
| $\text{Br}_2(l)$                | 152.3                    |
| $\text{Br}_2(g)$                | 245.3                    |
| $\text{I}_2(s)$                 | 116.7                    |
| $\text{I}_2(g)$                 | 260.6                    |
| C (diamond)                     | 2.4                      |
| C (graphite)                    | 5.69                     |
| $\text{CH}_4$ (methane)         | 186.2                    |
| $\text{C}_2\text{H}_6$ (ethane) | 229.5                    |
| $\text{He}(g)$                  | 126.1                    |
| $\text{Ne}(g)$                  | 146.2                    |

number of microstates for a macroscopic system containing many molecules. Instead, entropy is obtained by calorimetric methods. In fact, as we will see shortly, it is possible to determine the absolute value of entropy of a substance, called absolute entropy, something we cannot do for energy or enthalpy. *Standard entropy* is the absolute entropy of a substance at 1 atm and 25°C. (Recall that the standard state refers only to 1 atm. The reason for specifying 25°C is that many processes are carried out at room temperature.) Table 18.1 lists standard entropies of a few elements and compounds; Appendix 2 provides a more extensive listing. The units of entropy are J/K or J/K · mol for 1 mole of the substance. We use joules rather than kilojoules because entropy values are typically quite small. Entropies of elements and compounds are all positive (that is,  $S^\circ > 0$ ). By contrast, the standard enthalpy of formation ( $\Delta H_f^\circ$ ) for elements in their stable form is arbitrarily set equal to zero, and for compounds it may be positive or negative.

Referring to Table 18.1, we see that the standard entropy of water vapor is greater than that of liquid water. Similarly, bromine vapor has a higher standard entropy than liquid bromine, and iodine vapor has a greater standard entropy than solid iodine. For different substances in the same phase, molecular complexity determines which ones have higher entropies. Both diamond and graphite are solids, but diamond has a more ordered structure and hence a smaller number of microstates (see Figure 12.22). Therefore, diamond has a smaller standard entropy than graphite. Consider the natural gases methane and ethane. Ethane has a more complex structure and hence more ways to execute molecular motions, which also increase its microstates. Therefore, ethane has a greater standard entropy than methane. Both helium and neon are monatomic gases, which cannot execute rotational or vibrational motions, but neon has a greater standard entropy than helium because its molar mass is greater. Heavier atoms have more closely spaced energy levels so there is a greater distribution of the atoms' energy among the energy levels. Consequently, there are more microstates associated with these atoms.

**Example 18.1**

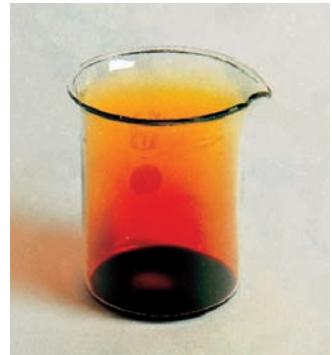
Predict whether the entropy change is greater or less than zero for each of the following processes: (a) freezing ethanol, (b) evaporating a beaker of liquid bromine at room temperature, (c) dissolving glucose in water, (d) cooling nitrogen gas from 80°C to 20°C.

*(Continued)*

**Strategy** To determine the entropy change in each case, we examine whether the number of microstates of the system increases or decreases. The sign of  $\Delta S$  will be positive if there is an increase in the number of microstates and negative if the number of microstates decreases.

- Solution**
- Upon freezing, the ethanol molecules are held rigidly in position. This phase transition reduces the number of microstates and therefore the entropy decreases; that is,  $\Delta S < 0$ .
  - Evaporating bromine increases the number of microstates because the  $\text{Br}_2$  molecules can occupy many more positions in nearly empty space. Therefore  $\Delta S > 0$ .
  - Glucose is a nonelectrolyte. The solution process leads to a greater dispersal of matter due to the mixing of glucose and water molecules so we expect  $\Delta S > 0$ .
  - The cooling process decreases various molecular motions. This leads to a decrease in microstates and so  $\Delta S < 0$ .

**Practice Exercise** How does the entropy of a system change for each of the following processes? (a) condensing water vapor, (b) forming sucrose crystals from a supersaturated solution, (c) heating hydrogen gas from  $60^\circ\text{C}$  to  $80^\circ\text{C}$ , and (d) subliming dry ice.



Bromine is a fuming liquid at room temperature.

**Similar problem:** 18.5.

## 18.4 The Second Law of Thermodynamics

The connection between entropy and the spontaneity of a reaction is expressed by the **second law of thermodynamics**: *The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.* Because the universe is made up of the system and the surroundings, the entropy change in the universe ( $\Delta S_{\text{univ}}$ ) for any process is the *sum* of the entropy changes in the system ( $\Delta S_{\text{sys}}$ ) and in the surroundings ( $\Delta S_{\text{surr}}$ ). Mathematically, we can express the second law of thermodynamics as follows:

$$\text{For a spontaneous process: } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \quad (18.4)$$

**Just talking about entropy increases its value in the universe.**

$$\text{For an equilibrium process: } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0 \quad (18.5)$$

For a spontaneous process, the second law says that  $\Delta S_{\text{univ}}$  must be greater than zero, but it does not place a restriction on either  $\Delta S_{\text{sys}}$  or  $\Delta S_{\text{surr}}$ . Thus, it is possible for either  $\Delta S_{\text{sys}}$  or  $\Delta S_{\text{surr}}$  to be negative, as long as the sum of these two quantities is greater than zero. For an equilibrium process,  $\Delta S_{\text{univ}}$  is zero. In this case,  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$  must be equal in magnitude, but opposite in sign. What if for some hypothetical process we find that  $\Delta S_{\text{univ}}$  is negative? What this means is that the process is not spontaneous in the direction described. Rather, it is spontaneous in the *opposite* direction.

### Entropy Changes in the System

To calculate  $\Delta S_{\text{univ}}$ , we need to know both  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$ . Let us focus first on  $\Delta S_{\text{sys}}$ . Suppose that the system is represented by the following reaction:



**Interactivity:**  
Entropies of Reactions  
ARIS, Interactives

As is the case for the enthalpy of a reaction [see Equation (6.17)], the *standard entropy of reaction*  $\Delta S_{\text{rxn}}^{\circ}$  is given by *the difference in standard entropies between products and reactants*:

$$\Delta S_{\text{rxn}}^{\circ} = [cS^{\circ}(\text{C}) + dS^{\circ}(\text{D})] - [aS^{\circ}(\text{A}) + bS^{\circ}(\text{B})] \quad (18.6)$$

or, in general, using  $\Sigma$  to represent summation and  $m$  and  $n$  for the stoichiometric coefficients in the reaction,

$$\Delta S_{\text{rxn}}^{\circ} = \Sigma nS^{\circ}(\text{products}) - \Sigma mS^{\circ}(\text{reactants}) \quad (18.7)$$

The standard entropy values of a large number of compounds have been measured in  $\text{J/K} \cdot \text{mol}$ . To calculate  $\Delta S_{\text{rxn}}^{\circ}$  (which is  $\Delta S_{\text{sys}}$ ), we look up their values in Appendix 2 and proceed according to Example 18.2.

### Example 18.2

From the standard entropy values in Appendix 2, calculate the standard entropy changes for the following reactions at 25°C.

- (a)  $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$
- (b)  $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$
- (c)  $\text{H}_2(g) + \text{Cl}_2(g) \longrightarrow 2\text{HCl}(g)$

**Strategy** To calculate the standard entropy of a reaction, we look up the standard entropies of reactants and products in Appendix 2 and apply Equation (18.7). As in the calculation of enthalpy of reaction [see Equation (6.18)], the stoichiometric coefficients have no units, so  $\Delta S_{\text{rxn}}^{\circ}$  is expressed in units of  $\text{J/K} \cdot \text{mol}$ .

#### Solution

$$\begin{aligned} \text{(a)} \quad \Delta S_{\text{rxn}}^{\circ} &= [S^{\circ}(\text{CaO}) + S^{\circ}(\text{CO}_2)] - [S^{\circ}(\text{CaCO}_3)] \\ &= [(39.8 \text{ J/K} \cdot \text{mol}) + (213.6 \text{ J/K} \cdot \text{mol})] - (92.9 \text{ J/K} \cdot \text{mol}) \\ &= 160.5 \text{ J/K} \cdot \text{mol} \end{aligned}$$

Thus, when 1 mole of  $\text{CaCO}_3$  decomposes to form 1 mole of  $\text{CaO}$  and 1 mole of gaseous  $\text{CO}_2$ , there is an increase in entropy equal to 160.5  $\text{J/K} \cdot \text{mol}$ .

$$\begin{aligned} \text{(b)} \quad \Delta S_{\text{rxn}}^{\circ} &= [2S^{\circ}(\text{NH}_3)] - [S^{\circ}(\text{N}_2) + 3S^{\circ}(\text{H}_2)] \\ &= (2)(193 \text{ J/K} \cdot \text{mol}) - [(192 \text{ J/K} \cdot \text{mol}) + (3)(131 \text{ J/K} \cdot \text{mol})] \\ &= -199 \text{ J/K} \cdot \text{mol} \end{aligned}$$

This result shows that when 1 mole of gaseous nitrogen reacts with 3 moles of gaseous hydrogen to form 2 moles of gaseous ammonia, there is a decrease in entropy equal to  $-199 \text{ J/K} \cdot \text{mol}$ .

$$\begin{aligned} \text{(c)} \quad \Delta S_{\text{rxn}}^{\circ} &= [2S^{\circ}(\text{HCl})] - [S^{\circ}(\text{H}_2) + S^{\circ}(\text{Cl}_2)] \\ &= (2)(187 \text{ J/K} \cdot \text{mol}) - [(131 \text{ J/K} \cdot \text{mol}) + (223 \text{ J/K} \cdot \text{mol})] \\ &= 20 \text{ J/K} \cdot \text{mol} \end{aligned}$$

Thus, the formation of 2 moles of gaseous HCl from 1 mole of gaseous  $\text{H}_2$  and 1 mole of gaseous  $\text{Cl}_2$  results in a small increase in entropy equal to 20  $\text{J/K} \cdot \text{mol}$ .

**Comment** The  $\Delta S_{\text{rxn}}^{\circ}$  values all apply to the system.

**Practice Exercise** Calculate the standard entropy change for the following reactions at 25°C:

- (a)  $2\text{CO}(g) + \text{O}_2(g) \longrightarrow 2\text{CO}_2(g)$
- (b)  $3\text{O}_2(g) \longrightarrow 2\text{O}_3(g)$
- (c)  $2\text{NaHCO}_3(s) \longrightarrow \text{Na}_2\text{CO}_3(s) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$

Similar problems: 18.11 and 18.12.

The results of Example 18.2 are consistent with those observed for many other reactions. Taken together, they support the following general rules:

- If a reaction produces more gas molecules than it consumes [Example 18.2(a)],  $\Delta S^\circ$  is positive.
- If the total number of gas molecules diminishes [Example 18.2(b)],  $\Delta S^\circ$  is negative.
- If there is no net change in the total number of gas molecules [Example 18.2(c)], then  $\Delta S^\circ$  may be positive or negative, but will be relatively small numerically.

We omit the subscript rxn for simplicity.

These conclusions make sense, given that gases invariably have greater entropy than liquids and solids. For reactions involving only liquids and solids, predicting the sign of  $\Delta S^\circ$  is more difficult, but in many such cases an increase in the total number of molecules and/or ions is accompanied by an increase in entropy.

### Example 18.3

Predict whether the entropy change of the system in each of the following reactions is positive or negative.

- $2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(l)$
- $\text{NH}_4\text{Cl}(s) \longrightarrow \text{NH}_3(g) + \text{HCl}(g)$
- $\text{H}_2(g) + \text{Br}_2(g) \longrightarrow 2\text{HBr}(g)$

**Strategy** We are asked to predict, not calculate, the sign of entropy change in the reactions. The factors that lead to an increase in entropy are (1) a transition from a condensed phase to the vapor phase and (2) a reaction that produces more product molecules than reactant molecules in the same phase. It is also important to compare the relative complexity of the product and reactant molecules. In general, the more complex the molecular structure, the greater the entropy of the compound.

- Solution**
- Two reactant molecules combine to form one product molecule. Even though  $\text{H}_2\text{O}$  is a more complex molecule than either  $\text{H}_2$  and  $\text{O}_2$ , the fact that there is a net decrease of one molecule and gases are converted to liquid ensures that the number of microstates will be diminished and hence  $\Delta S^\circ$  is negative.
  - A solid is converted to two gaseous products. Therefore,  $\Delta S^\circ$  is positive.
  - The same number of molecules is involved in the reactants as in the product. Furthermore, all molecules are diatomic and therefore of similar complexity. As a result, we cannot predict the sign of  $\Delta S^\circ$ , but we know that the change must be quite small in magnitude.

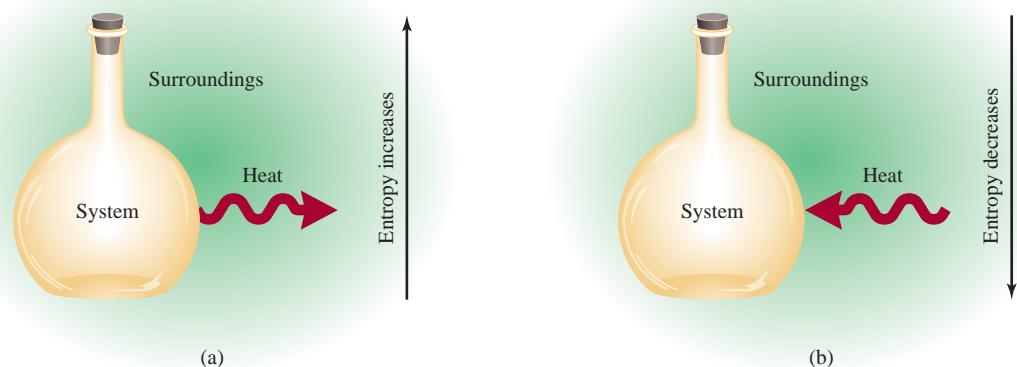
Similar problems: 18.13 and 18.14.

**Practice Exercise** Discuss qualitatively the sign of the entropy change expected for each of the following processes:

- $\text{I}_2(s) \longrightarrow 2\text{I}(g)$
- $2\text{Zn}(s) + \text{O}_2(g) \longrightarrow 2\text{ZnO}(s)$
- $\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2\text{NO}(g)$

## Entropy Changes in the Surroundings

Next we see how  $\Delta S_{\text{surr}}$  is calculated. When an exothermic process takes place in the system, the heat transferred to the surroundings enhances motion of the molecules in the surroundings. Consequently, there is an increase in the number of microstates and the entropy of the surroundings increases. Conversely, an endothermic process in the system absorbs heat from the surroundings and so decreases the

**Figure 18.5**

(a) An exothermic process transfers heat from the system to the surroundings and results in an increase in the entropy of the surroundings. (b) An endothermic process absorbs heat from the surroundings and thereby decreases the entropy of the surroundings.

entropy of the surroundings because molecular motion decreases (Figure 18.5). For constant-pressure processes, the heat change is equal to the enthalpy change of the system,  $\Delta H_{\text{sys}}$ . Therefore, the change in entropy of the surroundings,  $\Delta S_{\text{surr}}$ , is proportional to  $\Delta H_{\text{sys}}$ :

$$\Delta S_{\text{surr}} \propto -\Delta H_{\text{sys}}$$

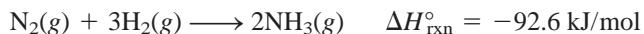
The minus sign is used because if the process is exothermic,  $\Delta H_{\text{sys}}$  is negative and  $\Delta S_{\text{surr}}$  is a positive quantity, indicating an increase in entropy. On the other hand, for an endothermic process,  $\Delta H_{\text{sys}}$  is positive and the negative sign ensures that the entropy of the surroundings decreases.

The change in entropy for a given amount of heat absorbed also depends on the temperature. If the temperature of the surroundings is high, the molecules are already quite energetic. Therefore, the absorption of heat from an exothermic process in the system will have relatively little impact on molecular motion and the resulting increase in entropy of the surroundings will be small. However, if the temperature of the surroundings is low, then the addition of the same amount of heat will cause a more drastic increase in molecular motion and hence a larger increase in entropy. By analogy, someone coughing in a crowded restaurant will not disturb too many people, but someone coughing in a library definitely will. From the inverse relationship between  $\Delta S_{\text{surr}}$  and temperature  $T$  (in kelvins)—that is, the higher the temperature, the smaller the  $\Delta S_{\text{surr}}$  and vice versa—we can rewrite the preceding relationship as

This equation, which can be derived from the laws of thermodynamics, assumes that both the system and the surroundings are at temperature  $T$ .

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \quad (18.8)$$

Let us now apply the procedure for calculating  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$  to the synthesis of ammonia and ask whether the reaction is spontaneous at 25°C:



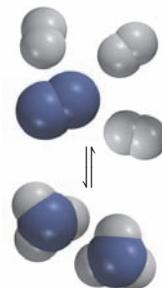
From Example 18.2(b) we have  $\Delta S_{\text{sys}} = -199 \text{ J/K} \cdot \text{mol}$ , and substituting  $\Delta H_{\text{sys}}$  ( $-92.6 \text{ kJ/mol}$ ) in Equation (18.8), we obtain

$$\Delta S_{\text{surr}} = \frac{-(-92.6 \times 1000) \text{ J/mol}}{298 \text{ K}} = 311 \text{ J/K} \cdot \text{mol}$$

The change in entropy of the universe is

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= -199 \text{ J/K} \cdot \text{mol} + 311 \text{ J/K} \cdot \text{mol} \\ &= 112 \text{ J/K} \cdot \text{mol}\end{aligned}$$

Because  $\Delta S_{\text{univ}}$  is positive, we predict that the reaction is spontaneous at  $25^\circ\text{C}$ . It is important to keep in mind that just because a reaction is spontaneous does not mean that it will occur at an observable rate. The synthesis of ammonia is, in fact, extremely slow at room temperature. Thermodynamics can tell us whether a reaction will occur spontaneously under specific conditions, but it does not say how fast it will occur. Reaction rates are the subject of chemical kinetics (see Chapter 14).



## The Third Law of Thermodynamics and Absolute Entropy

Finally, it is appropriate to consider the *third law of thermodynamics* briefly in connection with the determination of entropy values. So far we have related entropy to microstates—the greater the number of microstates a system possesses, the larger is the entropy of the system. Consider a perfect crystalline substance at absolute zero ( $0 \text{ K}$ ). Under these conditions, molecular motions are kept at a minimum and the number of microstates ( $W$ ) is one (there is only one way to arrange the atoms or molecules to form a perfect crystal). From Equation (18.1) we write

$$\begin{aligned}S &= k \ln W \\ &= k \ln 1 = 0\end{aligned}$$

According to the *third law of thermodynamics*, the entropy of a perfect crystalline substance is zero at the absolute zero of temperature. As the temperature increases, the freedom of motion increases and hence also the number of microstates. Thus, the entropy of any substance at a temperature above  $0 \text{ K}$  is greater than zero. Note also that if the crystal is impure or if it has defects, then its entropy is greater than zero even at  $0 \text{ K}$  because it would not be perfectly ordered and the number of microstates would be greater than one.

The important point about the third law of thermodynamics is that it enables us to determine the *absolute* entropies of substances. Starting with the knowledge that the entropy of a pure crystalline substance is zero at absolute zero, we can measure the increase in entropy of the substance when it is heated from  $0 \text{ K}$  to, say,  $298 \text{ K}$ . The change in entropy,  $\Delta S$ , is given by

$$\begin{aligned}\Delta S &= S_f - S_i \\ &= S_f\end{aligned}$$

because  $S_i$  is zero. The entropy of the substance at  $298 \text{ K}$ , then, is given by  $\Delta S$  or  $S_f$ , which is called the absolute entropy because this is the *true* value and not a value derived using some arbitrary reference as in the case of standard enthalpy of formation. Thus, the entropy values quoted so far and those listed in Appendix 2

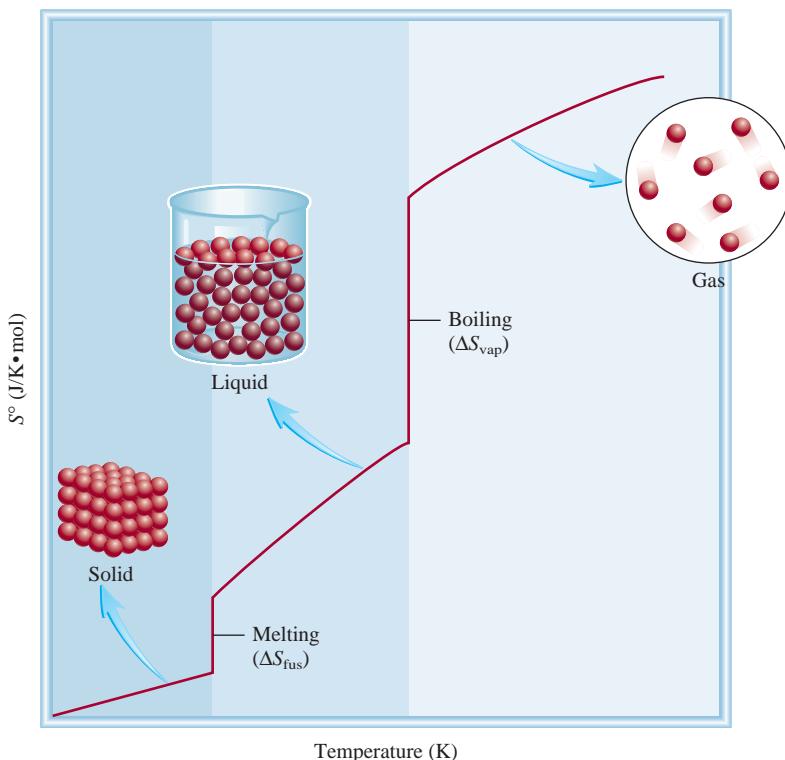


**Interactivity:**  
Entropy vs. Temperature  
ARIS, Interactives

The entropy increase can be calculated from the temperature change and heat capacity of the substance, plus any phase changes.

**Figure 18.6**

*Entropy increase of a substance as the temperature rises from absolute zero.*



are all absolute entropies. Because measurements are carried out at 1 atm, we usually refer to absolute entropies as standard entropies. In contrast, we cannot have the absolute energy or enthalpy of a substance because the zero of energy or enthalpy is undefined. Figure 18.6 shows the change (increase) in entropy of a substance with temperature. At absolute zero, it has a zero entropy value (assuming that it is a perfect crystalline substance). As it is heated, its entropy increases gradually because of greater molecular motion. At the melting point, there is a sizable increase in entropy as the liquid state is formed. Further heating increases the entropy of the liquid again due to enhanced molecular motion. At the boiling point there is a large increase in entropy as a result of the liquid-to-vapor transition. Beyond that temperature, the entropy of the gas continues to rise with increasing temperature.

## 18.5 Gibbs Free Energy

The second law of thermodynamics tells us that a spontaneous reaction increases the entropy of the universe; that is,  $\Delta S_{\text{univ}} > 0$ . In order to determine the sign of  $\Delta S_{\text{univ}}$  for a reaction, however, we would need to calculate both  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$ . In general, we are usually concerned only with what happens in a particular system. Therefore, we need another thermodynamic function to help us determine whether a reaction will occur spontaneously if we consider only the system itself.

From Equation (18.4), we know that for a spontaneous process, we have

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

Substituting  $-\Delta H_{\text{sys}}/T$  for  $\Delta S_{\text{surr}}$ , we write

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0$$

Multiplying both sides of the equation by  $T$  gives

$$T\Delta S_{\text{univ}} = -\Delta H_{\text{sys}} + T\Delta S_{\text{sys}} > 0$$

Now we have a criterion for a spontaneous reaction that is expressed only in terms of the properties of the system ( $\Delta H_{\text{sys}}$  and  $\Delta S_{\text{sys}}$ ) and we can ignore the surroundings. For convenience, we can change the preceding equation by multiplying it throughout by  $-1$  and replacing the  $>$  sign with  $<$ :

$$-T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$$

The change in unequal sign when we multiply the equation by  $-1$  follows from the fact that  $1 > 0$  and  $-1 < 0$ .

This equation says that for a process carried out at constant pressure and temperature  $T$ , if the changes in enthalpy and entropy of the system are such that  $\Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$  is less than zero, the process must be spontaneous.

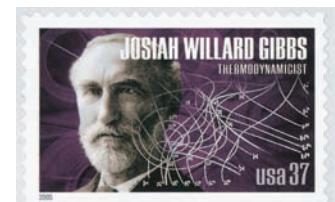
In order to express the spontaneity of a reaction more directly, we introduce another thermodynamic function called **Gibbs free energy** ( $G$ ), or simply **free energy** (after the American physicist Josiah Willard Gibbs):

$$G = H - TS \quad (18.9)$$

All quantities in Equation (18.9) pertain to the system, and  $T$  is the temperature of the system. You can see that  $G$  has units of energy (both  $H$  and  $TS$  are in energy units). Like  $H$  and  $S$ ,  $G$  is a state function.

The change in free energy ( $\Delta G$ ) of a system for a *constant-temperature* process is

$$\Delta G = \Delta H - T\Delta S \quad (18.10)$$



A commemorative stamp honoring Gibbs.

We omit the subscript  $\text{sys}$  for simplicity.

In this context free energy is *the energy available to do work*. Thus, if a particular reaction is accompanied by a release of usable energy (that is, if  $\Delta G$  is negative), this fact alone guarantees that it is spontaneous, and there is no need to worry about what happens to the rest of the universe.

The word "free" in the term "free energy" does not mean without cost.

Note that we have merely organized the expression for the entropy change of the universe and equating the free-energy change of the system ( $\Delta G$ ) with  $-T\Delta S_{\text{univ}}$ , so that we can focus on changes in the system. We can now summarize the conditions for spontaneity and equilibrium at constant temperature and pressure in terms of  $\Delta G$  as follows:

- $\Delta G < 0$  The reaction is spontaneous in the forward direction.
- $\Delta G > 0$  The reaction is nonspontaneous. The reaction is spontaneous in the opposite direction.
- $\Delta G = 0$  The system is at equilibrium. There is no net change.

## Standard Free-Energy Changes

The **standard free-energy of reaction** ( $\Delta G_{\text{rxn}}^{\circ}$ ) is *the free-energy change for a reaction when it occurs under standard-state conditions, when reactants in their standard states are converted to products in their standard states*. Table 18.2 summarizes the

**TABLE 18.2****Conventions for Standard States**

| State of Matter | Standard State         |
|-----------------|------------------------|
| Gas             | 1 atm pressure         |
| Liquid          | Pure liquid            |
| Solid           | Pure solid             |
| Elements*       | $\Delta G_f^\circ = 0$ |
| Solution        | 1 molar concentration  |

\*The most stable allotropic form at 25°C and 1 atm.

conventions used by chemists to define the standard states of pure substances as well as solutions. To calculate ( $\Delta G_{rxn}^\circ$ ) we start with the equation



The standard free-energy change for this reaction is given by

$$\Delta G_{rxn}^\circ = [c\Delta G_f^\circ(C) + d\Delta G_f^\circ(D)] - [a\Delta G_f^\circ(A) + b\Delta G_f^\circ(B)] \quad (18.11)$$

or, in general,

$$\Delta G_{rxn}^\circ = \sum n\Delta G_f^\circ(\text{products}) - \sum m\Delta G_f^\circ(\text{reactants}) \quad (18.12)$$

where  $m$  and  $n$  are stoichiometric coefficients. The term  $\Delta G_f^\circ$  is the **standard free energy of formation** of a compound, that is, *the free-energy change that occurs when 1 mole of the compound is synthesized from its elements in their standard states*. For the combustion of graphite:



the standard free-energy change [from Equation (18.12)] is

$$\Delta G_{rxn}^\circ = \Delta G_f^\circ(CO_2) - [\Delta G_f^\circ(C, \text{graphite}) + \Delta G_f^\circ(O_2)]$$

As in the case of the standard enthalpy of formation (p. 192), we define the standard free energy of formation of any element in its stable allotropic form at 1 atm and 25°C as zero. Thus,

$$\Delta G_f^\circ(C, \text{graphite}) = 0 \quad \text{and} \quad \Delta G_f^\circ(O_2) = 0$$

Therefore, the standard free-energy change for the reaction in this case is equal to the standard free energy of formation of  $CO_2$ :

$$\Delta G_{rxn}^\circ = \Delta G_f^\circ(CO_2)$$

Appendix 2 lists the values of  $\Delta G_f^\circ$  for a number of compounds.

**Example 18.4**

Calculate the standard free-energy changes for the following reactions at 25°C.

- (a)  $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$
- (b)  $2MgO(s) \longrightarrow 2Mg(s) + O_2(g)$

**Strategy** To calculate the standard free-energy change of a reaction, we look up the standard free energies of formation of reactants and products in Appendix 2 and apply Equation (18.12). Note that all the stoichiometric coefficients have no units so  $\Delta G_{rxn}^\circ$  is expressed in units of kJ/mol, and  $\Delta G_f^\circ$  for  $O_2$  is zero because it is the stable allotropic element at 1 atm and 25°C.

**Solution** (a) According to Equation (18.12), we write

$$\Delta G_{rxn}^\circ = [\Delta G_f^\circ(CO_2) + 2\Delta G_f^\circ(H_2O)] - [\Delta G_f^\circ(CH_4) + 2\Delta G_f^\circ(O_2)]$$

(Continued)

We insert the appropriate values from Appendix 2:

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= [(-394.4 \text{ kJ/mol}) + (2)(-237.2 \text{ kJ/mol})] - \\ &\quad [(-50.8 \text{ kJ/mol}) + (2)(0 \text{ kJ/mol})] \\ &= -818.0 \text{ kJ/mol}\end{aligned}$$

(b) The equation is

$$\Delta G_{\text{rxn}}^{\circ} = [2\Delta G_f^{\circ}(\text{Mg}) + \Delta G_f^{\circ}(\text{O}_2)] - [2\Delta G_f^{\circ}(\text{MgO})]$$

From data in Appendix 2 we write

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= [(2)(0 \text{ kJ/mol}) + (0 \text{ kJ/mol})] - [(2)(-569.6 \text{ kJ/mol})] \\ &= 1139 \text{ kJ/mol}\end{aligned}$$

**Similar problems:** 18.17 and 18.18.

**Practice Exercise** Calculate the standard free-energy changes for the following reactions at 25°C:

- (a)  $\text{H}_2(g) + \text{Br}_2(l) \longrightarrow 2\text{HBr}(g)$
- (b)  $2\text{C}_2\text{H}_6(g) + 7\text{O}_2(g) \longrightarrow 4\text{CO}_2(g) + 6\text{H}_2\text{O}(l)$

## Applications of Equation (18.10)

In order to predict the sign of  $\Delta G$ , according to Equation (18.10) we need to know both  $\Delta H$  and  $\Delta S$ . A negative  $\Delta H$  (an exothermic reaction) and a positive  $\Delta S$  (a reaction that results in an increase in the microstates of the system) tend to make  $\Delta G$  negative, although temperature may also influence the *direction* of a spontaneous reaction. The four possible outcomes of this relationship are:

- If both  $\Delta H$  and  $\Delta S$  are positive, then  $\Delta G$  will be negative only when the  $T\Delta S$  term is greater in magnitude than  $\Delta H$ . This condition is met when  $T$  is large.
- If  $\Delta H$  is positive and  $\Delta S$  is negative,  $\Delta G$  will always be positive, regardless of temperature.
- If  $\Delta H$  is negative and  $\Delta S$  is positive, then  $\Delta G$  will always be negative regardless of temperature.
- If  $\Delta H$  is negative and  $\Delta S$  is negative, then  $\Delta G$  will be negative only when  $T\Delta S$  is smaller in magnitude than  $\Delta H$ . This condition is met when  $T$  is small.

The temperatures that will cause  $\Delta G$  to be negative for the first and last cases depend on the actual values of  $\Delta H$  and  $\Delta S$  of the system. Table 18.3 summarizes the effects of the possibilities just described.

Before we apply the change in free energy to predict reaction spontaneity, it is useful to distinguish between  $\Delta G$  and  $\Delta G^{\circ}$ . Suppose we carry out a reaction in solution with all the reactants in their standard states (that is, all at 1 M concentration). As soon as the reaction starts, the standard-state condition no longer exists for the reactants or the products because their concentrations are different from 1 M. Under nonstandard state conditions, we must use the sign of  $\Delta G$  rather than that of  $\Delta G^{\circ}$  to predict the direction of the reaction. The sign of  $\Delta G^{\circ}$ , on the other hand, tells us whether the products or the reactants are favored when the reacting system reaches equilibrium. Thus, a negative value of  $\Delta G^{\circ}$  indicates that the reaction favors product formation whereas a positive value of  $\Delta G^{\circ}$  indicates that there will be more reactants than products at equilibrium.

**In Section 18.6 we will see an equation relating  $\Delta G^{\circ}$  to the equilibrium constant  $K$ .**

**TABLE 18.3** Factors Affecting the Sign of  $\Delta G$  in the Relationship  $\Delta G = \Delta H - T\Delta S$ 

| $\Delta H$ | $\Delta S$ | $\Delta G$   | Example   |
|------------|------------|--|---|
| +          | +          | Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction. | $2\text{HgO}(s) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$                    |
| +          | -          | $\Delta G$ is always positive. Reaction is spontaneous in the reverse direction at all temperatures.                         | $3\text{O}_2(g) \longrightarrow 2\text{O}_3(g)$                                   |
| -          | +          | $\Delta G$ is always negative. Reaction proceeds spontaneously at all temperatures.  | $2\text{H}_2\text{O}_2(l) \longrightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$ |
| -          | -          | Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.         | $\text{NH}_3(g) + \text{HCl}(g) \longrightarrow \text{NH}_4\text{Cl}(s)$          |

We will now consider two specific applications of Equation (18.10).

### Temperature and Chemical Reactions

Calcium oxide (CaO), also called quicklime, is an extremely valuable inorganic substance used in steelmaking, production of calcium metal, the paper industry, water treatment, and pollution control. It is prepared by decomposing limestone ( $\text{CaCO}_3$ ) in a kiln at a high temperature (Figure 18.7):



Le Châtelier's principle predicts that the forward, endothermic reaction is favored by heating.

The reaction is reversible, and CaO readily combines with  $\text{CO}_2$  to form  $\text{CaCO}_3$ . The pressure of  $\text{CO}_2$  in equilibrium with  $\text{CaCO}_3$  and CaO increases with temperature. In the industrial preparation of quicklime, the system is never maintained at equilibrium; rather,  $\text{CO}_2$  is constantly removed from the kiln to shift the equilibrium from left to right, promoting the formation of calcium oxide.

The important information for the practical chemist is the temperature at which the decomposition of  $\text{CaCO}_3$  becomes appreciable (that is, the temperature at which the reaction begins to favor products). We can make a reliable estimate of that temperature as follows. First we calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  for the reaction at  $25^\circ\text{C}$ , using the data in Appendix 2. To determine  $\Delta H^\circ$  we apply Equation (6.17):

$$\begin{aligned}\Delta H^\circ &= [\Delta H_f^\circ(\text{CaO}) + \Delta H_f^\circ(\text{CO}_2)] - [\Delta H_f^\circ(\text{CaCO}_3)] \\ &= [(-635.6 \text{ kJ/mol}) + (-393.5 \text{ kJ/mol})] - (-1206.9 \text{ kJ/mol}) \\ &= 177.8 \text{ kJ/mol}\end{aligned}$$

Next we apply Equation (18.6) to find  $\Delta S^\circ$

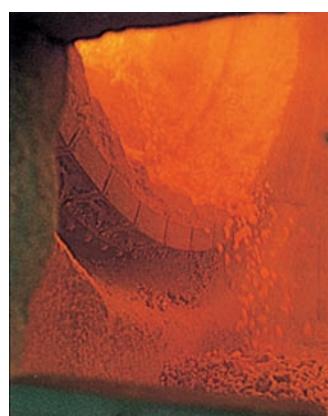
$$\begin{aligned}\Delta S^\circ &= [S^\circ(\text{CaO}) + S^\circ(\text{CO}_2)] - S^\circ(\text{CaCO}_3) \\ &= [(39.8 \text{ J/K} \cdot \text{mol}) + (213.6 \text{ J/K} \cdot \text{mol})] - (92.9 \text{ J/K} \cdot \text{mol}) \\ &= 160.5 \text{ J/K} \cdot \text{mol}\end{aligned}$$

From Equation (18.10)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

we obtain

$$\begin{aligned}\Delta G^\circ &= 177.8 \text{ kJ/mol} - (298 \text{ K})(160.5 \text{ J/K} \cdot \text{mol}) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) \\ &= 130.0 \text{ kJ/mol}\end{aligned}$$



**Figure 18.7**  
The production of CaO from  $\text{CaCO}_3$  in a rotatory kiln.

Because  $\Delta G^\circ$  is a large positive quantity, we conclude that the reaction is not favored for product formation at 25°C (or 298 K). Indeed, the pressure of CO<sub>2</sub> is so low at room temperature that it cannot be measured. In order to make  $\Delta G^\circ$  negative, we first have to find the temperature at which  $\Delta G^\circ$  is zero; that is,

$$0 = \Delta H^\circ - T\Delta S^\circ$$

or

$$\begin{aligned} T &= \frac{\Delta H^\circ}{\Delta S^\circ} \\ &= \frac{(177.8 \text{ kJ/mol})(1000 \text{ J/1 kJ})}{160.5 \text{ J/K} \cdot \text{mol}} \\ &= 1108 \text{ K or } 835^\circ\text{C} \end{aligned}$$

At a temperature higher than 835°C,  $\Delta G^\circ$  becomes negative, indicating that the reaction now favors the formation of CaO and CO<sub>2</sub>. For example, at 840°C, or 1113 K,

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 177.8 \text{ kJ/mol} - (1113 \text{ K})(160.5 \text{ J/K} \cdot \text{mol})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \\ &= -0.8 \text{ kJ/mol} \end{aligned}$$

Two points are worth making about such a calculation. First, we used the  $\Delta H^\circ$  and  $\Delta S^\circ$  values at 25°C to calculate changes that occur at a much higher temperature. Because both  $\Delta H^\circ$  and  $\Delta S^\circ$  change with temperature, this approach will not give us an accurate value of  $\Delta G^\circ$ , but it is good enough for “ball park” estimates. Second, we should not be misled into thinking that nothing happens below 835°C and that at 835°C CaCO<sub>3</sub> suddenly begins to decompose. Far from it. The fact that  $\Delta G^\circ$  is a positive value at some temperature below 835°C does not mean that no CO<sub>2</sub> is produced, but rather that the pressure of the CO<sub>2</sub> gas formed at that temperature will be below 1 atm (its standard-state value; see Table 18.2). As Figure 18.8 shows, the pressure of CO<sub>2</sub> at first increases very slowly with temperature; it becomes easily measurable above 700°C. The significance of 835°C is that this is the temperature at which the equilibrium pressure of CO<sub>2</sub> reaches 1 atm. Above 835°C, the equilibrium pressure of CO<sub>2</sub> exceeds 1 atm.

The equilibrium constant of this reaction is  $K_p = P_{\text{CO}_2}$ .

### Phase Transitions

At the temperature at which a phase transition occurs (that is, at the melting point or boiling point) the system is at equilibrium ( $\Delta G = 0$ ), so Equation (18.10) becomes

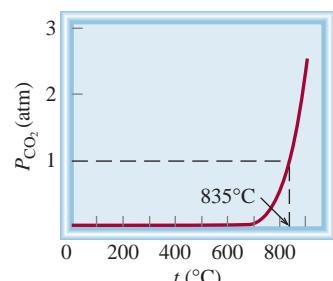
$$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ 0 &= \Delta H - T\Delta S \end{aligned}$$

or

$$\Delta S = \frac{\Delta H}{T}$$

Let us first consider the ice-water equilibrium. For the ice → water transition,  $\Delta H$  is the molar heat of fusion (see Table 12.7), and  $T$  is the melting point. The entropy change is therefore

$$\begin{aligned} \Delta S_{\text{ice} \rightarrow \text{water}} &= \frac{6010 \text{ J/mol}}{273 \text{ K}} \\ &= 22.0 \text{ J/K} \cdot \text{mol} \end{aligned}$$



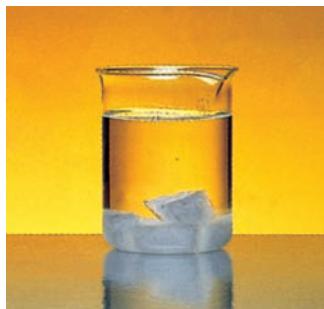
**Figure 18.8**  
Equilibrium pressure of CO<sub>2</sub> from the decomposition of CaCO<sub>3</sub>, as a function of temperature. This curve is calculated by assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  of the reaction do not change with temperature.

Thus, when 1 mole of ice melts at 0°C, there is an increase in entropy of 22.0 J/K · mol. The increase in entropy is consistent with the increase in microstates from solid to liquid. Conversely, for the water → ice transition, the decrease in entropy is given by

The melting of ice is an endothermic process ( $\Delta H$  is positive), and the freezing of water is exothermic ( $\Delta H$  is negative).

$$\begin{aligned}\Delta S_{\text{water} \rightarrow \text{ice}} &= \frac{-6010 \text{ J/mol}}{273 \text{ K}} \\ &= -22.0 \text{ J/K · mol}\end{aligned}$$

In the laboratory we normally carry out unidirectional changes, that is, either ice to water or water to ice transition. We can calculate entropy change in each case using the equation  $\Delta S = \Delta H/T$  as long as the temperature remains at 0°C. The same procedure can be applied to the water → steam transition. In this case  $\Delta H$  is the heat of vaporization and  $T$  is the boiling point of water.



Liquid and solid benzene in equilibrium at 5.5°C.

### Example 18.5

The molar heats of fusion and vaporization of benzene are 10.9 kJ/mol and 31.0 kJ/mol, respectively. Calculate the entropy changes for the solid → liquid and liquid → vapor transitions for benzene. At 1 atm pressure, benzene melts at 5.5°C and boils at 80.1°C.

**Strategy** At the melting point, liquid and solid benzene are at equilibrium, so  $\Delta G = 0$ . From Equation (18.10) we have  $\Delta G = 0 = \Delta H - T\Delta S$  or  $\Delta S = \Delta H/T$ . To calculate the entropy change for the solid benzene → liquid benzene transition, we write  $\Delta S_{\text{fus}} = \Delta H_{\text{fus}}/T_f$ . Here  $\Delta H_{\text{fus}}$  is positive for an endothermic process, so  $\Delta S_{\text{fus}}$  is also positive, as expected for a solid to liquid transition. The same procedure applies to the liquid benzene → vapor benzene transition. What temperature unit should be used?

**Solution** The entropy change for melting 1 mole of benzene at 5.5°C is

$$\begin{aligned}\Delta S_{\text{fus}} &= \frac{\Delta H_{\text{fus}}}{\Delta T_f} \\ &= \frac{(10.9 \text{ kJ/mol})(1000 \text{ J/1 kJ})}{(5.5 + 273) \text{ K}} \\ &= 39.1 \text{ J/K · mol}\end{aligned}$$

Similarly, the entropy change for boiling 1 mole of benzene at 80.1°C is

$$\begin{aligned}\Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_{\text{bp}}} \\ &= \frac{(31.0 \text{ kJ/mol})(1000 \text{ J/1 kJ})}{(80.1 + 273) \text{ K}} \\ &= 87.8 \text{ J/K · mol}\end{aligned}$$

**Check** Because vaporization creates more microstates than the melting process,  $\Delta S_{\text{vap}} > \Delta S_{\text{fus}}$ .

Similar problem: 18.60.

**Practice Exercise** The molar heats of fusion and vaporization of argon are 1.3 kJ/mol and 6.3 kJ/mol, and argon's melting point and boiling point are  $-190^\circ\text{C}$  and  $-186^\circ\text{C}$ , respectively. Calculate the entropy changes for fusion and vaporization.

## 18.6 Free Energy and Chemical Equilibrium

As mentioned earlier, during the course of a chemical reaction not all the reactants and products will be at their standard states. Under this condition, the relationship between  $\Delta G$  and  $\Delta G^\circ$ , which can be derived from thermodynamics, is

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (18.13)$$

where  $R$  is the gas constant ( $8.314 \text{ J/K} \cdot \text{mol}$ ),  $T$  is the absolute temperature of the reaction, and  $Q$  is the reaction quotient (see p. 507). We see that  $\Delta G$  depends on two quantities:  $\Delta G^\circ$  and  $RT \ln Q$ . For a given reaction at temperature  $T$  the value of  $\Delta G^\circ$  is fixed but that of  $RT \ln Q$  is not, because  $Q$  varies according to the composition of the reaction mixture. Let us consider two special cases:

**Case 1:** A large negative value of  $\Delta G^\circ$  will tend to make  $\Delta G$  also negative. Thus, the net reaction will proceed from left to right until a significant amount of product has been formed. At that point, the  $RT \ln Q$  term will become positive enough to match the negative  $\Delta G^\circ$  term.

**Case 2:** A large positive  $\Delta G^\circ$  term will tend to make  $\Delta G$  also positive. Thus, the net reaction will proceed from right to left until a significant amount of reactant has been formed. At that point, the  $RT \ln Q$  term will become negative enough to match the positive  $\Delta G^\circ$  term.

At equilibrium, by definition,  $\Delta G = 0$  and  $Q = K$ , where  $K$  is the equilibrium constant. Thus,

$$0 = \Delta G^\circ + RT \ln K$$

or

$$\Delta G^\circ = -RT \ln K \quad (18.14)$$

In this equation,  $K_P$  is used for gases and  $K_c$  for reactions in solution. Note that the larger the  $K$  is, the more negative  $\Delta G^\circ$  is. For chemists, Equation (18.14) is one of the most important equations in thermodynamics because it enables us to find the equilibrium constant of a reaction if we know the change in standard free energy and vice versa.

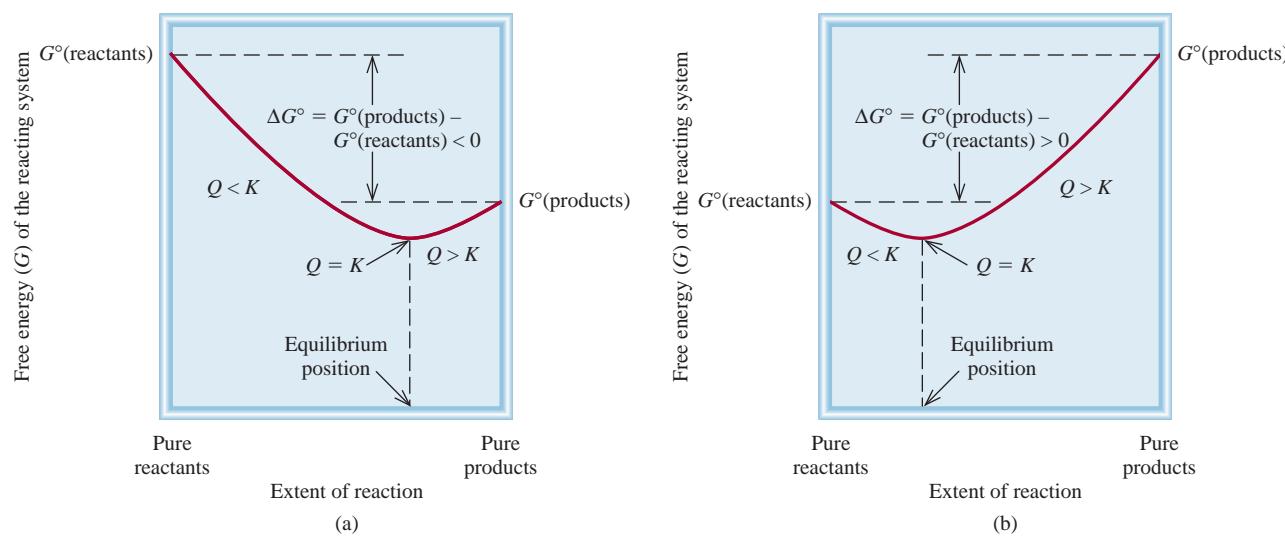
It is significant that Equation (18.14) relates the equilibrium constant to the *standard* free energy change  $\Delta G^\circ$  rather than to the *actual* free energy change  $\Delta G$ . The actual free energy change of the system varies as the reaction progresses and becomes zero at equilibrium. On the other hand,  $\Delta G^\circ$  is a constant for a particular reaction at a given temperature. Figure 18.9 shows plots of the free energy of a reacting system versus the extent of the reaction for two types of reactions. As you can see, if  $\Delta G^\circ < 0$ , the products are favored over reactants at equilibrium. Conversely, if  $\Delta G^\circ > 0$ , there will be more reactants than products at equilibrium. Table 18.4 summarizes the three possible relations between  $\Delta G^\circ$  and  $K$ , as predicted by Equation (18.14). Remember this important distinction: It is the sign of  $\Delta G$  and not that of  $\Delta G^\circ$  that determines the direction of reaction spontaneity. The sign of  $\Delta G^\circ$  tells us only the relative amounts of products and reactants when equilibrium is reached, not the direction of the net reaction.

For reactions having very large or very small equilibrium constants, it is generally very difficult, if not impossible, to measure the  $K$  values by monitoring the

Sooner or later a reversible reaction will reach equilibrium.

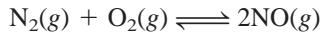


**Interactivity:**  
Free Energy—Equilibrium  
ARIS, Interactives

**Figure 18.9**

(a)  $\Delta G^\circ < 0$ . At equilibrium, there is a significant conversion of reactants to products. (b)  $\Delta G^\circ > 0$ . At equilibrium, reactants are favored over products. In both cases, the net reaction toward equilibrium is from left to right (reactants to products) if  $Q < K$  and right to left (products to reactants) if  $Q > K$ .

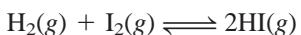
concentrations of all the reacting species. Consider, for example, the formation of nitric oxide from molecular nitrogen and molecular oxygen:



At 25°C, the equilibrium constant  $K_P$  is

$$K_P = \frac{P_{\text{NO}}^2}{P_{\text{N}_2} P_{\text{O}_2}} = 4.0 \times 10^{-31}$$

The very small value of  $K_P$  means that the concentration of NO at equilibrium will be exceedingly low. In such a case the equilibrium constant is more conveniently obtained from  $\Delta G^\circ$ . (As we have seen,  $\Delta G^\circ$  can be calculated from  $\Delta H^\circ$  and  $\Delta S^\circ$ .) On the other hand, the equilibrium constant for the formation of hydrogen iodide from molecular hydrogen and molecular iodine is near unity at room temperature:



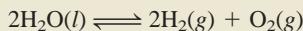
For this reaction it is easier to measure  $K_P$  and then calculate  $\Delta G^\circ$  using Equation (18.14) than to measure  $\Delta H^\circ$  and  $\Delta S^\circ$  and use Equation (18.10).

**TABLE 18.4** Relation Between  $\Delta G^\circ$  and  $K$  as Predicted by the Equation  $\Delta G^\circ = -RT \ln K$

| $K$   | $\ln K$  | $\Delta G^\circ$ | Comments   |
|-------|----------|------------------|--|
| $> 1$ | Positive | Negative         | Products are favored over reactants at equilibrium.        |
| $= 1$ | 0        | 0                | Products and reactants are equally favored at equilibrium. |
| $< 1$ | Negative | Positive         | Reactants are favored over products at equilibrium.        |

### Example 18.6

Using data listed in Appendix 2, calculate the equilibrium constant ( $K_P$ ) for the following reaction at 25°C:



**Strategy** According to Equation (18.14), the equilibrium constant for the reaction is related to the standard free energy change; that is,  $\Delta G^\circ = -RT \ln K$ . Therefore, we first need to calculate  $\Delta G^\circ$  by following the procedure in Example 18.4. Then we can calculate  $K_P$ . What temperature unit should be used?

**Solution** According to Equation (18.12),

$$\begin{aligned}\Delta G_{\text{rxn}}^\circ &= [2\Delta G_f^\circ(\text{H}_2) + \Delta G_f^\circ(\text{O}_2)] - [2\Delta G_f^\circ(\text{H}_2\text{O})] \\ &= [(2)(0 \text{ kJ/mol}) + (0 \text{ kJ/mol})] - [(2)(-237.2 \text{ kJ/mol})] \\ &= 474.4 \text{ kJ/mol}\end{aligned}$$

Using Equation (18.14)

$$\begin{aligned}\Delta G_{\text{rxn}}^\circ &= -RT \ln K_P \\ 474.4 \text{ kJ/mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}} &= -(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \ln K_P \\ \ln K_P &= -191.5 \\ K_P &= e^{-191.5} = 7 \times 10^{-84}\end{aligned}$$

**Comment** This extremely small equilibrium constant is consistent with the fact that water does not decompose into hydrogen and oxygen gases at 25°C. Thus, a large positive  $\Delta G^\circ$  favors reactants over products at equilibrium.

To calculate  $K_P$ , enter  $-191.5$  on your calculator and then press the key labeled “e” or “inv(verse) ln x.”

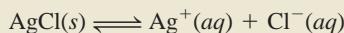
Similar problems: 18.23 and 18.26.

**Practice Exercise** Calculate the equilibrium constant ( $K_P$ ) for the reaction at 25°C



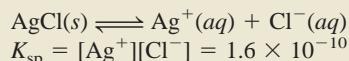
### Example 18.7

In Chapter 17 we discussed the solubility product of slightly soluble substances. Using the solubility product of silver chloride at 25°C ( $1.6 \times 10^{-10}$ ), calculate  $\Delta G^\circ$  for the process



**Strategy** According to Equation (18.14), the equilibrium constant for the reaction is related to standard free energy change; that is,  $\Delta G^\circ = -RT \ln K$ . Because this is a heterogeneous equilibrium, the solubility product ( $K_{\text{sp}}$ ) is the equilibrium constant. We calculate the standard free energy change from the  $K_{\text{sp}}$  value of AgCl. What temperature unit should be used?

**Solution** The solubility equilibrium for AgCl is



Using Equation (18.14) we obtain

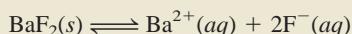
$$\begin{aligned}\Delta G^\circ &= -(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \ln (1.6 \times 10^{-10}) \\ &= 5.6 \times 10^4 \text{ J/mol} \\ &= 56 \text{ kJ/mol}\end{aligned}$$

(Continued)

**Similar problem:** 18.25.

**Check** The large, positive  $\Delta G^\circ$  indicates that AgCl is slightly soluble and that the equilibrium lies mostly to the left.

**Practice Exercise** Calculate  $\Delta G^\circ$  for the following process at 25°C:



The  $K_{sp}$  of BaF<sub>2</sub> is  $1.7 \times 10^{-6}$ .

### Example 18.8

The equilibrium constant ( $K_P$ ) for the reaction



is 0.113 at 298 K, which corresponds to a standard free-energy change of 5.40 kJ/mol. In a certain experiment, the initial pressures are  $P_{\text{NO}_2} = 0.122$  atm and  $P_{\text{N}_2\text{O}_4} = 0.453$  atm. Calculate  $\Delta G$  for the reaction at these pressures and predict the direction of the net reaction.

**Strategy** From the information given we see that neither the reactant nor the product is at its standard state of 1 atm. To determine the direction of the net reaction, we need to calculate the free-energy change under nonstandard-state conditions ( $\Delta G$ ) using Equation (18.13) and the given  $\Delta G^\circ$  value. Note that the partial pressures are expressed as dimensionless quantities in the reaction quotient  $Q_P$ .

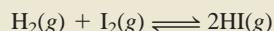
**Solution** Equation (18.13) can be written as

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q_P \\ &= \Delta G^\circ + RT \ln \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} \\ &= 5.40 \times 10^3 \text{ J/mol} + (8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \times \ln \frac{(0.122)^2}{0.453} \\ &= 5.40 \times 10^3 \text{ J/mol} - 8.46 \times 10^3 \text{ J/mol} \\ &= -3.06 \times 10^3 \text{ J/mol} = -3.06 \text{ kJ/mol}\end{aligned}$$

Because  $\Delta G < 0$ , the net reaction proceeds from left to right to reach equilibrium.

**Check** Note that although  $\Delta G^\circ > 0$ , the reaction can be made to favor product formation initially by having a small concentration (pressure) of the product compared to that of the reactant. Confirm the prediction by showing that  $Q_P < K_P$ .

**Practice Exercise** The  $\Delta G^\circ$  for the reaction



is 2.60 kJ/mol at 25°C. In one experiment, the initial pressures are  $P_{\text{H}_2} = 4.26$  atm,  $P_{\text{I}_2} = 0.024$  atm, and  $P_{\text{HI}} = 0.23$  atm. Calculate  $\Delta G$  for the reaction and predict the direction of the net reaction.

## 18.7 Thermodynamics in Living Systems

Many biochemical reactions have a positive  $\Delta G^\circ$  value, yet they are essential to the maintenance of life. In living systems these reactions are coupled to an energetically favorable process, one that has a negative  $\Delta G^\circ$  value. The principle of *coupled*

**Similar problems:** 18.27 and 18.28.

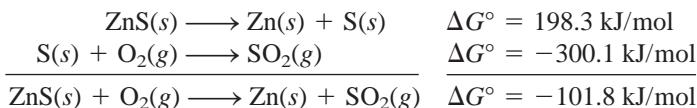
*reactions* is based on a simple concept: we can use a thermodynamically favorable reaction to drive an unfavorable one. Consider an industrial process. Suppose we wish to extract zinc from the ore sphalerite ( $\text{ZnS}$ ). The following reaction will not work because it has a large positive  $\Delta G^\circ$  value:



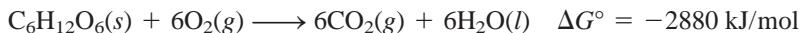
On the other hand, the combustion of sulfur to form sulfur dioxide is favored because of its large negative  $\Delta G^\circ$  value:



By coupling the two processes we can bring about the separation of zinc from zinc sulfide. In practice, this means heating  $\text{ZnS}$  in air so that the tendency of S to form  $\text{SO}_2$  will promote the decomposition of  $\text{ZnS}$ :



Coupled reactions play a crucial role in our survival. In biological systems, enzymes facilitate a wide variety of nonspontaneous reactions. For example, in the human body, food molecules, represented by glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ), are converted to carbon dioxide and water during metabolism with a substantial release of free energy:

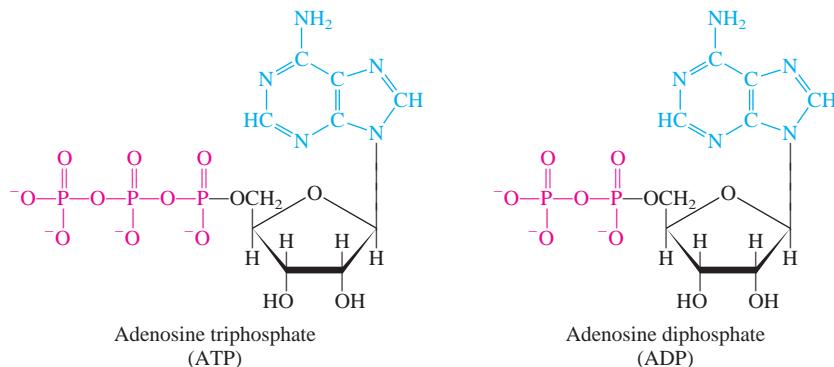


In a living cell, this reaction does not take place in a single step (as burning glucose in a flame would); rather, the glucose molecule is broken down with the aid of enzymes in a series of steps. Much of the free energy released along the way is used to synthesize adenosine triphosphate (ATP) from adenosine diphosphate (ADP) and phosphoric acid (Figure 18.10):



The function of ATP is to store free energy until it is needed by cells. Under appropriate conditions, ATP undergoes hydrolysis to give ADP and phosphoric acid, with a release of 31 kJ of free energy, which can be used to drive energetically unfavorable reactions, such as protein synthesis.

Proteins are polymers made of amino acids. The stepwise synthesis of a protein molecule involves the joining of individual amino acids. Consider the formation of

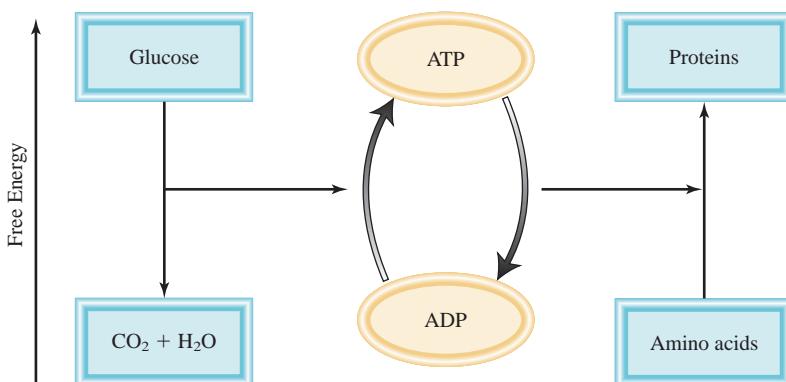


A mechanical analog for coupled reactions. We can make the smaller weight move upward (a nonspontaneous process) by coupling it with the falling of a larger weight.

**Figure 18.10**  
Structure of ATP and ADP in ionized forms. The adenine group is in blue, the ribose group in black, and the phosphate group in red. Note that ADP has one fewer phosphate group than ATP.

**Figure 18.11**

Schematic representation of ATP synthesis and coupled reactions in living systems. The conversion of glucose to carbon dioxide and water during metabolism releases free energy. The released free energy is used to convert ADP into ATP. The ATP molecules are then used as an energy source to drive unfavorable reactions, such as protein synthesis from amino acids.



the dipeptide (a two-amino-acid unit) alanylglycine from alanine and glycine. This reaction represents the first step in the synthesis of a protein molecule:



As you can see, this reaction does not favor the formation of product, and so only a little of the dipeptide would be formed at equilibrium. However, with the aid of an enzyme, the reaction is coupled to the hydrolysis of ATP as follows:



The overall free-energy change is given by  $\Delta G^\circ = -31 \text{ kJ/mol} + 29 \text{ kJ/mol} = -2 \text{ kJ/mol}$ , which means that the coupled reaction now favors the formation of product, and an appreciable amount of alanylglucine will be formed under this condition. Figure 18.11 shows the ATP-ADP interconversions that act as energy storage (from metabolism) and free energy release (from ATP hydrolysis) to drive essential reactions.

## KEY EQUATIONS

$$S = k \ln W \quad (18.1) \quad \text{Relating entropy to number of microstates.}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \quad (18.4) \quad \text{The second law of thermodynamics (spontaneous process).}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0 \quad (18.5) \quad \text{The second law of thermodynamics (equilibrium process).}$$

$$\Delta S_{\text{rxn}}^\circ = \sum n S^\circ(\text{products}) - \sum m S^\circ(\text{reactants}) \quad (18.7) \quad \text{Standard entropy change of a reaction.}$$

$$G = H - TS \quad (18.9) \quad \text{Definition of Gibbs free energy.}$$

$$\Delta G = \Delta H - T\Delta S \quad (18.10) \quad \text{Free-energy change at constant temperature.}$$

$$\Delta G_{\text{rxn}}^\circ = \sum n \Delta G_f^\circ(\text{products}) - \sum m \Delta G_f^\circ(\text{reactants}) \quad (18.12) \quad \text{Standard free-energy change of a reaction.}$$

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (18.13) \quad \text{Relationship between free-energy change and standard free-energy change and reaction quotient.}$$

$$\Delta G^\circ = -RT \ln K \quad (18.14) \quad \text{Relationship between standard free-energy change and the equilibrium constant.}$$

## SUMMARY OF FACTS AND CONCEPTS

- Entropy is usually described as a measure of the disorder of a system. Any spontaneous process must lead to a net increase in entropy in the universe (second law of thermodynamics).
- The standard entropy of a chemical reaction can be calculated from the absolute entropies of reactants and products.
- The third law of thermodynamics states that the entropy of a perfect crystalline substance is zero at 0 K. This law enables us to measure the absolute entropies of substances.
- Under conditions of constant temperature and pressure, the free-energy change  $\Delta G$  is less than zero for a spontaneous process and greater than zero for a nonspontaneous process. For an equilibrium process,  $\Delta G = 0$ .
- For a chemical or physical process at constant temperature and pressure,  $\Delta G = \Delta H - T\Delta S$ . This equation can be used to predict the spontaneity of a process.
- The standard free-energy change for a reaction,  $\Delta G^\circ$ , can be calculated from the standard free energies of formation of reactants and products.
- The equilibrium constant of a reaction and the standard free-energy change of the reaction are related by the equation  $\Delta G^\circ = -RT \ln K$ .
- Many biological reactions are nonspontaneous. They are driven by the hydrolysis of ATP, for which  $\Delta G^\circ$  is negative.

## KEY WORDS

Entropy ( $S$ ), p. 612  
 Free energy ( $G$ ), p. 623  
 Gibbs free energy ( $G$ ), p. 623

Second law of thermodynamics, p. 617  
 Standard entropy of reaction ( $\Delta S_{rxn}^\circ$ ), p. 618

Standard free energy of formation ( $\Delta G_f^\circ$ ), p. 624  
 Standard free energy of reaction ( $\Delta G_{rxn}^\circ$ ), p. 623

Third law of thermodynamics, p. 621

## QUESTIONS AND PROBLEMS

### Spontaneous Processes and Entropy

#### Review Questions

- Explain what is meant by a spontaneous process. Give two examples each of spontaneous and non-spontaneous processes.
- Which of the following processes are spontaneous and which are nonspontaneous? (a) dissolving table salt (NaCl) in hot soup; (b) climbing Mt. Everest; (c) spreading fragrance in a room by removing the cap from a perfume bottle; (d) separating helium and neon from a mixture of the gases
- Which of the following processes are spontaneous and which are nonspontaneous at a given temperature?
  - $\text{NaNO}_3(s) \xrightarrow{\text{H}_2\text{O}} \text{NaNO}_3(aq)$  saturated soln
  - $\text{NaNO}_3(s) \xrightarrow{\text{H}_2\text{O}} \text{NaNO}_3(aq)$  unsaturated soln
  - $\text{NaNO}_3(s) \xrightarrow{\text{H}_2\text{O}} \text{NaNO}_3(aq)$  supersaturated soln
- Define entropy. What are the units of entropy?

- How does the entropy of a system change for each of the following processes?

- A solid melts.
- A liquid freezes.
- A liquid boils.
- A vapor is converted to a solid.
- A vapor condenses to a liquid.
- A solid sublimes.
- Urea dissolves in water.

#### Problems

- Consider the situation shown in Figure 18.1(a). After the valve is opened, the probability of finding one molecule in either bulb is  $\frac{1}{2}$  (because the bulbs have the same volume) and that of finding the molecule in the total volume is one. The probability of finding two molecules in the same bulb is the product of the individual probabilities; that is,  $\frac{1}{2} \times \frac{1}{2}$  or  $\frac{1}{4}$ . Extend

the calculation to finding 100 molecules in the same bulb. Based on your results, explain why it is highly improbable for the process shown in Figure 18.1(b) to occur spontaneously when the number of molecules becomes very large, say,  $6 \times 10^{23}$ .

## The Second Law of Thermodynamics

### Review Questions

- 18.7 State the second law of thermodynamics in words and express it mathematically.
- 18.8 State the third law of thermodynamics and explain its usefulness in calculating entropy values.

### Problems

- 18.9 For each pair of substances listed here, choose the one having the larger standard entropy value at 25°C. The same molar amount is used in the comparison. Explain the basis for your choice. (a) Li(s) or Li(l); (b) C<sub>2</sub>H<sub>5</sub>OH(l) or CH<sub>3</sub>OCH<sub>3</sub>(l) (*Hint:* Which molecule can hydrogen-bond?); (c) Ar(g) or Xe(g); (d) CO(g) or CO<sub>2</sub>(g); (e) O<sub>2</sub>(g) or O<sub>3</sub>(g); (f) NO<sub>2</sub>(g) or N<sub>2</sub>O<sub>4</sub>(g)

- 18.10** Arrange the following substances (1 mole each) in order of increasing entropy at 25°C: (a) Ne(g), (b) SO<sub>2</sub>(g), (c) Na(s), (d) NaCl(s), (e) H<sub>2</sub>(g). Give the reasons for your arrangement.

- 18.11 Using the data in Appendix 2, calculate the standard entropy changes for the following reactions at 25°C:
  - (a) S(s) + O<sub>2</sub>(g) → SO<sub>2</sub>(g)
  - (b) MgCO<sub>3</sub>(s) → MgO(s) + CO<sub>2</sub>(g)

- 18.12** Using the data in Appendix 2, calculate the standard entropy changes for the following reactions at 25°C:
  - (a) H<sub>2</sub>(g) + CuO(s) → Cu(s) + H<sub>2</sub>O(g)
  - (b) 2Al(s) + 3ZnO(s) → Al<sub>2</sub>O<sub>3</sub>(s) + 3Zn(s)
  - (c) CH<sub>4</sub>(g) + 2O<sub>2</sub>(g) → CO<sub>2</sub>(g) + 2H<sub>2</sub>O(l)

- 18.13 Without consulting Appendix 2, predict whether the entropy change is positive or negative for each of the following reactions. Give reasons for your predictions.
  - (a) 2KClO<sub>4</sub>(s) → 2KClO<sub>3</sub>(s) + O<sub>2</sub>(g)
  - (b) H<sub>2</sub>O(g) → H<sub>2</sub>O(l)
  - (c) 2Na(s) + 2H<sub>2</sub>O(l) → 2NaOH(aq) + H<sub>2</sub>(g)
  - (d) N<sub>2</sub>(g) → 2N(g)

- 18.14** State whether the sign of the entropy change expected for each of the following processes will be positive or negative, and explain your predictions.
  - (a) PCl<sub>3</sub>(l) + Cl<sub>2</sub>(g) → PCl<sub>5</sub>(s)
  - (b) 2HgO(s) → 2Hg(l) + O<sub>2</sub>(g)
  - (c) H<sub>2</sub>(g) → 2H(g)
  - (d) U(s) + 3F<sub>2</sub>(g) → UF<sub>6</sub>(s)

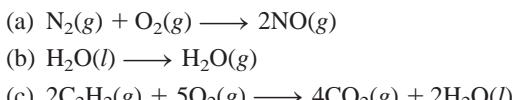
## Gibbs Free Energy

### Review Questions

- 18.15 Define free energy. What are its units?
- 18.16 Why is it more convenient to predict the direction of a reaction in terms of  $\Delta G_{\text{sys}}$  instead of  $\Delta S_{\text{univ}}$ ? Under what conditions can  $\Delta G_{\text{sys}}$  be used to predict the spontaneity of a reaction?

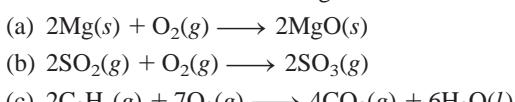
### Problems

- 18.17 Calculate  $\Delta G^\circ$  for the following reactions at 25°C:



(*Hint:* Look up the standard free energies of formation of the reactants and products in Appendix 2.)

- 18.18** Calculate  $\Delta G^\circ$  for the following reactions at 25°C:



See Appendix 2 for thermodynamic data.

- 18.19 From the values of  $\Delta H$  and  $\Delta S$ , predict which of the following reactions would be spontaneous at 25°C: Reaction A:  $\Delta H = 10.5 \text{ kJ/mol}$ ,  $\Delta S = 30 \text{ J/K} \cdot \text{mol}$ ; reaction B:  $\Delta H = 1.8 \text{ kJ/mol}$ ,  $\Delta S = -113 \text{ J/K} \cdot \text{mol}$ . If either of the reactions is nonspontaneous at 25°C, at what temperature might it become spontaneous?

- 18.20** Find the temperatures at which reactions with the following  $\Delta H$  and  $\Delta S$  values would become spontaneous: (a)  $\Delta H = -126 \text{ kJ/mol}$ ,  $\Delta S = 84 \text{ J/K} \cdot \text{mol}$ ; (b)  $\Delta H = -11.7 \text{ kJ/mol}$ ,  $\Delta S = -105 \text{ J/K} \cdot \text{mol}$ .

## Free Energy and Chemical Equilibrium

### Review Questions

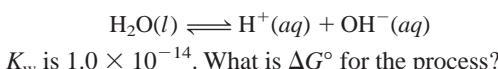
- 18.21 Explain the difference between  $\Delta G$  and  $\Delta G^\circ$ .
- 18.22 Explain why Equation (18.14) is of great importance in chemistry.

### Problems

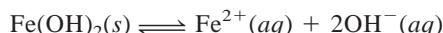
- 18.23 Calculate  $K_P$  for the following reaction at 25°C:



- 18.24** For the autoionization of water at 25°C,

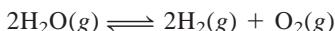


- 18.25 Consider the following reaction at 25°C:



Calculate  $\Delta G^\circ$  for the reaction.  $K_{\text{sp}}$  for  $\text{Fe(OH)}_2$  is  $1.6 \times 10^{-14}$ .

- 18.26** Calculate  $\Delta G^\circ$  and  $K_P$  for the following equilibrium reaction at 25°C.



- 18.27** (a) Calculate  $\Delta G^\circ$  and  $K_P$  for the following equilibrium reaction at 25°C. The  $\Delta G_f^\circ$  values are 0 for  $\text{Cl}_2(g)$ , -286 kJ/mol for  $\text{PCl}_3(g)$ , and -325 kJ/mol for  $\text{PCl}_5(g)$ .



- (b) Calculate  $\Delta G$  for the reaction if the partial pressures of the initial mixture are  $P_{\text{PCl}_5} = 0.0029$  atm,  $P_{\text{PCl}_3} = 0.27$  atm, and  $P_{\text{Cl}_2} = 0.40$  atm.

- 18.28** The equilibrium constant ( $K_P$ ) for the reaction



is 4.40 at 2000 K. (a) Calculate  $\Delta G^\circ$  for the reaction.

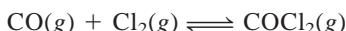
(b) Calculate  $\Delta G$  for the reaction when the partial pressures are  $P_{\text{H}_2} = 0.25$  atm,  $P_{\text{CO}_2} = 0.78$  atm,  $P_{\text{H}_2\text{O}} = 0.66$  atm, and  $P_{\text{CO}} = 1.20$  atm.

- 18.29** Consider the decomposition of calcium carbonate:



Calculate the pressure in atm of  $\text{CO}_2$  in an equilibrium process (a) at 25°C and (b) at 800°C. Assume that  $\Delta H^\circ = 177.8$  kJ/mol and  $\Delta S^\circ = 160.5 \text{ J/K} \cdot \text{mol}$  for the temperature range.

- 18.30** The equilibrium constant  $K_P$  for the reaction



is  $5.62 \times 10^{35}$  at 25°C. Calculate  $\Delta G_f^\circ$  for  $\text{COCl}_2$  at 25°C.

- 18.31** At 25°C,  $\Delta G^\circ$  for the process



is 8.6 kJ/mol. Calculate the vapor pressure of water at this temperature.

- 18.32** Calculate  $\Delta G^\circ$  for the process



Is the formation of graphite from diamond favored at 25°C? If so, why is it that diamonds do not become graphite on standing?

## Thermodynamics in Living Systems

### Review Questions

- 18.33** What is a coupled reaction? What is its importance in biological reactions?

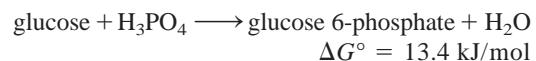
- 18.34** What is the role of ATP in biological reactions?

### Problems

- 18.35** Referring to the metabolic process involving glucose on p. 633, calculate the maximum number of moles

of ATP that can be synthesized from ADP from the breakdown of one mole of glucose.

- 18.36** In the metabolism of glucose, the first step is the conversion of glucose to glucose 6-phosphate:



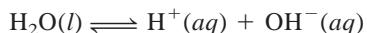
Because  $\Delta G^\circ$  is positive, this reaction does not favor the formation of products. Show how this reaction can be made to proceed by coupling it with the hydrolysis of ATP. Write an equation for the coupled reaction and estimate the equilibrium constant for the coupled process.

## Additional Problems

- 18.37** Explain the following nursery rhyme in terms of the second law of thermodynamics.

Humpty Dumpty sat on a wall;  
Humpty Dumpty had a great fall.  
All the King's horses and all the King's men  
Couldn't put Humpty together again.

- 18.38** Calculate  $\Delta G$  for the reaction



at 25°C for the following conditions:

- (a)  $[\text{H}^+] = 1.0 \times 10^{-7} \text{ M}$ ,  $[\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$
- (b)  $[\text{H}^+] = 1.0 \times 10^{-3} \text{ M}$ ,  $[\text{OH}^-] = 1.0 \times 10^{-4} \text{ M}$
- (c)  $[\text{H}^+] = 1.0 \times 10^{-12} \text{ M}$ ,  $[\text{OH}^-] = 2.0 \times 10^{-8} \text{ M}$
- (d)  $[\text{H}^+] = 3.5 \text{ M}$ ,  $[\text{OH}^-] = 4.8 \times 10^{-4} \text{ M}$

- 18.39** Which of the following thermodynamic functions are associated only with the first law of thermodynamics:  $S$ ,  $E$ ,  $G$ , and  $H$ ?

- 18.40** A student placed 1 g of each of three compounds A, B, and C in a container and found that after 1 week no change had occurred. Offer some possible explanations for the fact that no reactions took place. Assume that A, B, and C are totally miscible liquids.

- 18.41** Give a detailed example of each of the following, with an explanation: (a) a thermodynamically spontaneous process; (b) a process that would violate the first law of thermodynamics; (c) a process that would violate the second law of thermodynamics; (d) an irreversible process; (e) an equilibrium process.

- 18.42** Predict the signs of  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  of the system for the following processes at 1 atm: (a) ammonia melts at -60°C, (b) ammonia melts at -77.7°C, (c) ammonia melts at -100°C. (The normal melting point of ammonia is -77.7°C.)

- 18.43** Consider the following facts: Water freezes spontaneously at -5°C and 1 atm, and ice has a more ordered structure than liquid water. Explain how a spontaneous process can lead to a decrease in entropy.

- 18.44** Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) dissolves spontaneously and endothermically in water. What can you deduce about the sign of  $\Delta S$  for the solution process?

- 18.45** Calculate the equilibrium pressure of  $\text{CO}_2$  due to the decomposition of barium carbonate ( $\text{BaCO}_3$ ) at  $25^\circ\text{C}$ .

- 18.46** (a) Trouton's rule states that the ratio of the molar heat of vaporization of a liquid ( $\Delta H_{\text{vap}}$ ) to its boiling point in kelvins is approximately  $90 \text{ J/K} \cdot \text{mol}$ . Use the following data to show that this is the case and explain why Trouton's rule holds true:

|         | $t_{\text{bp}} (\text{°C})$ | $\Delta H_{\text{vap}} (\text{kJ/mol})$ |
|---------|-----------------------------|---|
| Benzene | 80.1                        | 31.0                                    |
| Hexane  | 68.7                        | 30.8                                    |
| Mercury | 357                         | 59.0                                    |
| Toluene | 110.6                       | 35.2                                    |

- (b) Use the values in Table 12.5 to calculate the same ratio for ethanol and water. Explain why Trouton's rule does not apply to these two substances as well as it does to other liquids.

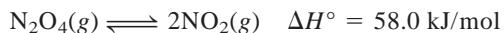
- 18.47** Referring to Problem 18.46, explain why the ratio is considerably smaller than  $90 \text{ J/K} \cdot \text{mol}$  for liquid HF.

- 18.48** Carbon monoxide (CO) and nitric oxide (NO) are polluting gases contained in automobile exhaust. Under suitable conditions, these gases can be made to react to form nitrogen ( $\text{N}_2$ ) and the less harmful carbon dioxide ( $\text{CO}_2$ ). (a) Write an equation for this reaction. (b) Identify the oxidizing and reducing agents. (c) Calculate the  $K_P$  for the reaction at  $25^\circ\text{C}$ . (d) Under normal atmospheric conditions, the partial pressures are  $P_{\text{N}_2} = 0.80 \text{ atm}$ ,  $P_{\text{CO}_2} = 3.0 \times 10^{-4} \text{ atm}$ ,  $P_{\text{CO}} = 5.0 \times 10^{-5} \text{ atm}$ , and  $P_{\text{NO}} = 5.0 \times 10^{-7} \text{ atm}$ . Calculate  $Q_P$  and predict the direction toward which the reaction will proceed. (e) Will raising the temperature favor the formation of  $\text{N}_2$  and  $\text{CO}_2$ ?

- 18.49** For reactions carried out under standard-state conditions, Equation (18.10) takes the form  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ . (a) Assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature, derive the equation

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

where  $K_1$  and  $K_2$  are the equilibrium constants at  $T_1$  and  $T_2$ , respectively. (b) Given that at  $25^\circ\text{C}$   $K_c = 4.63 \times 10^{-3}$  for the reaction



calculate the equilibrium constant at  $65^\circ\text{C}$ .

- 18.50** The  $K_{\text{sp}}$  of  $\text{AgCl}$  is given in Table 17.2. What is its value at  $60^\circ\text{C}$ ? [Hint: You need the result of Problem 18.49(a) and the data in Appendix 2 to calculate  $\Delta H^\circ$ .]

- 18.51** Under what conditions does a substance have a standard entropy of zero? Can a substance ever have a negative standard entropy?

- 18.52** Water gas, a mixture of  $\text{H}_2$  and CO, is a fuel made by reacting steam with red-hot coke (a by-product of coal distillation):



From the data in Appendix 2, estimate the temperature at which the reaction begins to favor the formation of products.

- 18.53** Consider the following Brønsted acid-base reaction at  $25^\circ\text{C}$ :



(a) Predict whether  $K$  will be greater or smaller than unity. (b) Does  $\Delta S^\circ$  or  $\Delta H^\circ$  make a greater contribution to  $\Delta G^\circ$ ? (c) Is  $\Delta H^\circ$  likely to be positive or negative?

- 18.54** Crystallization of sodium acetate from a supersaturated solution occurs spontaneously (see p. 426). What can you deduce about the signs of  $\Delta S$  and  $\Delta H$ ?

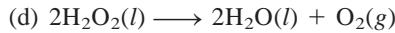
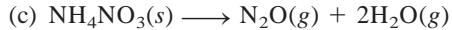
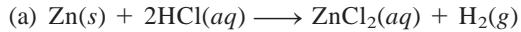
- 18.55** Consider the thermal decomposition of  $\text{CaCO}_3$ :



The equilibrium vapor pressures of  $\text{CO}_2$  are  $22.6 \text{ mmHg}$  at  $700^\circ\text{C}$  and  $1829 \text{ mmHg}$  at  $950^\circ\text{C}$ . Calculate the standard enthalpy of the reaction. [Hint: See Problem 18.49(a).]

- 18.56** A certain reaction is spontaneous at  $72^\circ\text{C}$ . If the enthalpy change for the reaction is  $19 \text{ kJ/mol}$ , what is the minimum value of  $\Delta S$  (in  $\text{J/K} \cdot \text{mol}$ ) for the reaction?

- 18.57** Predict whether the entropy change is positive or negative for each of these reactions:



- 18.58** The reaction  $\text{NH}_3(g) + \text{HCl}(g) \longrightarrow \text{NH}_4\text{Cl}(s)$  proceeds spontaneously at  $25^\circ\text{C}$  even though there is a decrease in the number of microstates of the system (gases are converted to a solid). Explain.

- 18.59** Use the following data to determine the normal boiling point, in kelvins, of mercury. What assumptions must you make in order to do the calculation?

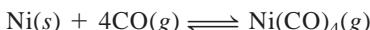
$$\begin{aligned} \text{Hg}(l): \quad \Delta H_f^\circ &= 0 \text{ (by definition)} \\ &S^\circ = 77.4 \text{ J/K} \cdot \text{mol} \end{aligned}$$

$$\begin{aligned} \text{Hg}(g): \quad \Delta H_f^\circ &= 60.78 \text{ kJ/mol} \\ &S^\circ = 174.7 \text{ J/K} \cdot \text{mol} \end{aligned}$$

- 18.60** The molar heat of vaporization of ethanol is  $39.3 \text{ kJ/mol}$  and the boiling point of ethanol is  $78.3^\circ\text{C}$ . Calculate  $\Delta S$  for the vaporization of  $0.50 \text{ mol}$  ethanol.

- 18.61 A certain reaction is known to have a  $\Delta G^\circ$  value of  $-122 \text{ kJ/mol}$ . Will the reaction necessarily occur if the reactants are mixed together?

- 18.62** In the Mond process for the purification of nickel, carbon monoxide is reacted with heated nickel to produce  $\text{Ni}(\text{CO})_4$ , which is a gas and can therefore be separated from solid impurities:



Given that the standard free energies of formation of  $\text{CO}(g)$  and  $\text{Ni}(\text{CO})_4(g)$  are  $-137.3 \text{ kJ/mol}$  and  $-587.4 \text{ kJ/mol}$ , respectively, calculate the equilibrium constant of the reaction at  $80^\circ\text{C}$ . Assume that  $\Delta G_f^\circ$  is temperature independent.

- 18.63 Calculate  $\Delta G^\circ$  and  $K_P$  for the following processes at  $25^\circ\text{C}$ :

- (a)  $\text{H}_2(g) + \text{Br}_2(l) \rightleftharpoons 2\text{HBr}(g)$   
 (b)  $\frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{Br}_2(l) \rightleftharpoons \text{HBr}(g)$

Account for the differences in  $\Delta G^\circ$  and  $K_P$  obtained for (a) and (b).

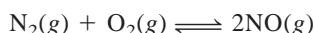
- 18.64** Calculate the pressure of  $\text{O}_2$  (in atm) over a sample of  $\text{NiO}$  at  $25^\circ\text{C}$  if  $\Delta G^\circ = 212 \text{ kJ/mol}$  for the reaction



- 18.65 Comment on the statement: “Just talking about entropy increases its value in the universe.”

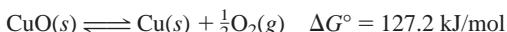
- 18.66** For a reaction with a negative  $\Delta G^\circ$  value, which of the following statements is false? (a) The equilibrium constant  $K$  is greater than one, (b) the reaction is spontaneous when all the reactants and products are in their standard states, and (c) the reaction is always exothermic.

- 18.67 Consider the reaction



Given that  $\Delta G^\circ$  for the reaction at  $25^\circ\text{C}$  is  $173.4 \text{ kJ/mol}$ , (a) calculate the standard free energy of formation of  $\text{NO}$ , and (b) calculate  $K_P$  of the reaction. (c) One of the starting substances in smog formation is  $\text{NO}$ . Assuming that the temperature in a running automobile engine is  $1100^\circ\text{C}$ , estimate  $K_P$  for the above reaction. (d) As farmers know, lightning helps to produce a better crop. Why?

- 18.68** Heating copper(II) oxide at  $400^\circ\text{C}$  does not produce any appreciable amount of Cu:



However, if this reaction is coupled to the conversion of graphite to carbon monoxide, it becomes spontaneous. Write an equation for the coupled process and calculate the equilibrium constant for the coupled reaction.

- 18.69 The internal combustion engine of a 1200-kg car is designed to run on octane ( $\text{C}_8\text{H}_{18}$ ), whose enthalpy of combustion is  $5510 \text{ kJ/mol}$ . If the car is moving up a slope, calculate the maximum height (in meters) to

which the car can be driven on 1.0 gallon of the fuel. Assume that the engine cylinder temperature is  $2200^\circ\text{C}$  and the exit temperature is  $760^\circ\text{C}$ , and neglect all forms of friction. The mass of 1 gallon of fuel is 3.1 kg. [Hint: The efficiency of the internal combustion engine, defined as work performed by the engine divided by the energy input, is given by  $(T_2 - T_1)/T_2$ , where  $T_2$  and  $T_1$  are the engine's operating temperature and exit temperature (in kelvins). The work done in moving the car over a vertical distance is  $mgh$ , where  $m$  is the mass of the car in kg,  $g$  the acceleration due to gravity ( $9.81 \text{ m/s}^2$ ), and  $h$  the height in meters.]

- 18.70** A carbon monoxide (CO) crystal is found to have entropy greater than zero at absolute zero of temperature. Give two possible explanations for this observation.

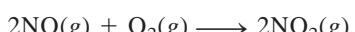
- 18.71 (a) Over the years there have been numerous claims about “perpetual motion machines,” machines that will produce useful work with no input of energy. Explain why the first law of thermodynamics prohibits the possibility of such a machine existing. (b) Another kind of machine, sometimes called a “perpetual motion of the second kind,” operates as follows. Suppose an ocean liner sails by scooping up water from the ocean and then extracting heat from the water, converting the heat to electric power to run the ship, and dumping the water back into the ocean. This process does not violate the first law of thermodynamics, for no energy is created—energy from the ocean is just converted to electrical energy. Show that the second law of thermodynamics prohibits the existence of such a machine.

- 18.72** The activity series in Section 4.4 shows that reaction (a) is spontaneous while reaction (b) is nonspontaneous at  $25^\circ\text{C}$ :

- (a)  $\text{Fe}(s) + 2\text{H}^+ \longrightarrow \text{Fe}^{2+}(aq) + \text{H}_2(g)$   
 (b)  $\text{Cu}(s) + 2\text{H}^+ \longrightarrow \text{Cu}^{2+}(aq) + \text{H}_2(g)$

Use the data in Appendix 2 to calculate the equilibrium constant for these reactions and hence confirm that the activity series is correct.

- 18.73 The rate constant for the elementary reaction



is  $7.1 \times 10^9/\text{M}^2 \cdot \text{s}$  at  $25^\circ\text{C}$ . What is the rate constant for the reverse reaction at the same temperature?

- 18.74** The following reaction was described as the cause of sulfur deposits formed at volcanic sites:



It may also be used to remove  $\text{SO}_2$  from powerplant stack gases. (a) Identify the type of redox reaction it is. (b) Calculate the equilibrium constant ( $K_P$ ) at  $25^\circ\text{C}$  and comment on whether this method is feasible for removing  $\text{SO}_2$ . (c) Would this procedure become more or less effective at a higher temperature?

- 18.75 Describe two ways that you could measure  $\Delta G^\circ$  of a reaction.

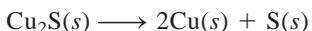
- 18.76** The following reaction represents the removal of ozone in the stratosphere:



Calculate the equilibrium constant ( $K_P$ ) for the reaction. In view of the magnitude of the equilibrium constant, explain why this reaction is not considered a major cause of ozone depletion in the absence of man-made pollutants such as the nitrogen oxides and CFCs? Assume the temperature of the stratosphere to be  $-30^\circ\text{C}$  and  $\Delta G_f^\circ$  to be temperature independent.

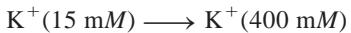
- 18.77 A 74.6-g ice cube floats in the Arctic Sea. The temperature and pressure of the system and surroundings are at 1 atm and  $0^\circ\text{C}$ . Calculate  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{surr}}$ , and  $\Delta S_{\text{univ}}$  for the melting of the ice cube. What can you conclude about the nature of the process from the value of  $\Delta S_{\text{univ}}$ ? (The molar heat of fusion of water is 6.01 kJ/mol.)

- 18.78** Comment on the feasibility of extracting copper from its ore chalcocite ( $\text{Cu}_2\text{S}$ ) by heating:



Calculate the  $\Delta G^\circ$  for the overall reaction if the above process is coupled to the conversion of sulfur to sulfur dioxide, given that  $\Delta G_f^\circ(\text{Cu}_2\text{S}) = -86.1$  kJ/mol.

- 18.79 Active transport is the process in which a substance is transferred from a region of lower concentration to one of higher concentration. This is a nonspontaneous process and must be coupled to a spontaneous process, such as the hydrolysis of ATP. The concentrations of  $\text{K}^+$  ions in the blood plasma and in nerve cells are 15 mM and 400 mM, respectively ( $1\text{ mM} = 1 \times 10^{-3}\text{ M}$ ). Use Equation (18.13) to calculate  $\Delta G$  for the process at the physiological temperature of  $37^\circ\text{C}$ :



In this calculation, the  $\Delta G^\circ$  term can be set to zero. What is the justification for this step?

- 18.80** Large quantities of hydrogen are needed for the synthesis of ammonia. One preparation of hydrogen involves the reaction between carbon monoxide and steam at  $300^\circ\text{C}$  in the presence of a copper-zinc catalyst:



Calculate the equilibrium constant ( $K_P$ ) for the reaction and the temperature at which the reaction favors the formation of CO and  $\text{H}_2\text{O}$ . Will a larger  $K_P$  be attained at the same temperature if a more efficient catalyst is used?

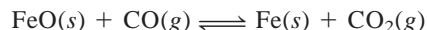
- 18.81 Consider two carboxylic acids (acids that contain the  $-\text{COOH}$  group):  $\text{CH}_3\text{COOH}$  (acetic acid,  $K_a = 1.8 \times 10^{-5}$ ) and  $\text{CH}_2\text{ClCOOH}$  (chloroacetic

acid,  $K_a = 1.4 \times 10^{-3}$ ). (a) Calculate  $\Delta G^\circ$  for the ionization of these acids at  $25^\circ\text{C}$  (b) From the equation  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ , we see that the contributions to the  $\Delta G^\circ$  term are an enthalpy term ( $\Delta H^\circ$ ) and a temperature times entropy term ( $T\Delta S^\circ$ ). These contributions are listed below for the two acids:

|                            | $\Delta H^\circ(\text{kJ/mol})$ | $T\Delta S^\circ(\text{kJ/mol})$ |
|----------------------------|---------------------------------|----------------------------------|
| $\text{CH}_3\text{COOH}$   | -0.57                           | -27.6                            |
| $\text{CH}_2\text{ClCOOH}$ | -4.7                            | -21.1                            |

Which is the dominant term in determining the value of  $\Delta G^\circ$  (and hence  $K_a$  of the acid)? (c) What processes contribute to  $\Delta H^\circ$ ? (Consider the ionization of the acids as a Brønsted acid-base reaction.) (d) Explain why the  $T\Delta S^\circ$  term is more negative for  $\text{CH}_3\text{COOH}$ .

- 18.82** One of the steps in the extraction of iron from its ore ( $\text{FeO}$ ) is the reduction of iron(II) oxide by carbon monoxide at  $900^\circ\text{C}$ :



If CO is allowed to react with an excess of  $\text{FeO}$ , calculate the mole fractions of CO and  $\text{CO}_2$  at equilibrium. State any assumptions.

- 18.83 Derive the following equation

$$\Delta G = RT \ln(Q/K)$$

where  $Q$  is the reaction quotient and describe how you would use it to predict the spontaneity of a reaction.

- 18.84** The sublimation of carbon dioxide at  $-78^\circ\text{C}$  is given by



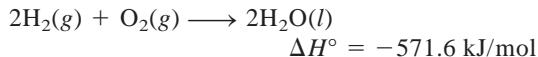
Calculate  $\Delta S_{\text{sub}}$  when 84.8 g of  $\text{CO}_2$  sublimes at this temperature.

- 18.85 Entropy has sometimes been described as “time’s arrow” because it is the property that determines the forward direction of time. Explain.

- 18.86** Referring to Figure 18.1, we see that the probability of finding all 100 molecules in the same flask is  $8 \times 10^{-31}$  (see Problem 18.6). Assuming that the age of the universe is 13 billion years, calculate the time in seconds during which this event can be observed.

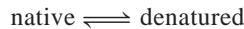
- 18.87 A student looked up the  $\Delta G_f^\circ$ ,  $\Delta H_f^\circ$ , and  $S^\circ$  values for  $\text{CO}_2$  in Appendix 2. Plugging these values into Equation (18.10), he found that  $\Delta G_f^\circ \neq \Delta H_f^\circ - TS^\circ$  at 298 K. What is wrong with his approach?

- 18.88** Consider the following reaction at 298 K:



Calculate  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{surr}}$ , and  $\Delta S_{\text{univ}}$  for the reaction.

- 18.89 As an approximation, we can assume that proteins exist either in the native (or physiologically functioning) state and the denatured state



The standard molar enthalpy and entropy of the denaturation of a certain protein are 512 kJ/mol and 1.60 J/K · mol, respectively. Comment on the signs and magnitudes of these quantities, and calculate the temperature at which the process favors the denatured state.

- 18.90** Which of the following are not state functions:  $S$ ,  $H$ ,  $q$ ,  $w$ ,  $T$ ?
- 18.91** Which of the following is not accompanied by an increase in the entropy of the system? (a) mixing of

two gases at the same temperature and pressure, (b) mixing of ethanol and water, (c) discharging a battery, (d) expansion of a gas followed by compression to its original temperature, pressure, and volume.

- 18.92** Hydrogenation reactions (for example, the process of converting C=C bonds to C—C bonds in food industry) are facilitated by the use of a transition metal catalyst, such as Ni or Pt. The initial step is the adsorption, or binding, of hydrogen gas onto the metal surface. Predict the signs of  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  when hydrogen gas is adsorbed onto the surface of Ni metal.

## SPECIAL PROBLEMS

- 18.93** The standard free energies of formation ( $\Delta G_f^\circ$ ) of the three isomers of pentane (see p. 358) in the gas phase are:  $n$ -pentane: −8.37 kJ/mol; 2-methylbutane: −14.8 kJ/mol; 2,2-dimethylpropane: −15.2 kJ/mol. (a) Determine the mole percent of these molecules in an equilibrium mixture at 25°C. (b) How does the stability of these molecules depend on the extent of branching?
- 18.94** Carry out the following experiments: Quickly stretch a rubber band (at least 0.5 cm wide) and press it against your lips. You will feel a warming effect. Next, carry out the reverse procedure; that is, first stretch a rubber band and hold it in position for a few seconds. Now quickly release the tension and press the rubber band against your lips. You will feel a cooling effect. (a) Apply Equation (18.7) to these processes to determine the signs of  $\Delta G$ ,  $\Delta H$ , and hence  $\Delta S$  in each case. (b) From the signs of  $\Delta S$ , what can you conclude about the structure of rubber molecules?
- 18.95** At 0 K, the entropy of carbon monoxide crystal is not zero but has a value of 4.2 J/K · mol, called the residual entropy. According to the third law of thermodynamics, this means that the crystal does not have a perfect arrangement of the CO molecules. (a) What would be the residual entropy if the arrangement were totally random? (b) Comment on the difference between the result in (a) and 4.2 J/K · mol [Hint: Assume that each CO molecule has two choices for orientation and use Equation (18.1) to calculate the residual entropy.]

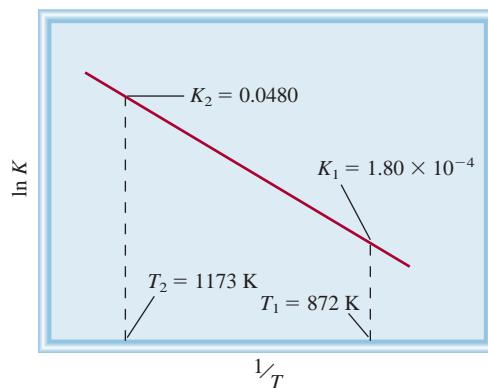
- 18.96** Comment on the correctness of the analogy sometimes used to relate a student's dormitory room becoming untidy to an increase in entropy.
- 18.97** The standard enthalpy of formation and the standard entropy of gaseous benzene are 82.93 kJ/mol and 269.2 J/K · mol, respectively. Calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  for the process at 25°C. Comment on your answers.



- 18.98** The following diagram shows the variation of the equilibrium constant with temperature for the reaction



Calculate  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  for the reaction at 872 K. (Hint: See Problem 18.49.)



## ANSWERS TO PRACTICE EXERCISES

- 18.1** (a) Entropy decreases, (b) entropy decreases, (c) entropy increases, (d) entropy increases.
- 18.2** (a) −173.6 J/K · mol, (b) −139.8 J/K · mol, (c) 215.3 J/K · mol. **18.3** (a)  $\Delta S > 0$ , (b)  $\Delta S < 0$ , (c)  $\Delta S \approx 0$ .

- 18.4** (a) −106.4 kJ/mol, (b) −2935.0 kJ/mol.

- 18.5**  $\Delta S_{\text{fus}} = 16 \text{ J/K} \cdot \text{mol}$ ;  $\Delta S_{\text{vap}} = 72 \text{ J/K} \cdot \text{mol}$ .

- 18.6**  $2 \times 10^{57}$ . **18.7** 33 kJ/mol. **18.8**  $\Delta G = 0.97 \text{ kJ/mol}$ ; direction is from right to left.



Hydrogen gas generated from an illuminated photoelectrode. Using light energy to produce hydrogen from water can play an important role in the development of fuel cells.

## Redox Reactions and Electrochemistry

### CHAPTER OUTLINE

- 19.1** Redox Reactions 643  
Balancing Redox Equations
- 19.2** Galvanic Cells 646
- 19.3** Standard Reduction Potentials 648
- 19.4** Thermodynamics of Redox Reactions 654
- 19.5** The Effect of Concentration on Cell Emf 657  
The Nernst Equation • Concentration Cells
- 19.6** Batteries 661  
The Dry Cell Battery • The Mercury Battery • The Lead Storage Battery • The Lithium-Ion Battery • Fuel Cells
- 19.7** Corrosion 665
- 19.8** Electrolysis 668  
Electrolysis of Molten Sodium Chloride • Electrolysis of Water • Electrolysis of an Aqueous Sodium Chloride Solution • Quantitative Aspects of Electrolysis
- 19.9** Electrometallurgy 673  
Production of Aluminum Metal • Purification of Copper Metal



### Interactive Activity Summary

1. Interactivity: Redox Reactions—Oxidation States for Nitrogen (19.1)
2. Interactivity: Redox Reactions—Oxidized or Reduced? (19.1)
3. Animation: Galvanic Cells (19.2)

### ESSENTIAL CONCEPTS

**Redox Reactions and Electrochemical Cells** Equations representing redox reactions can be balanced using the half-reaction method. These reactions involve the transfer of electrons from a reducing agent to an oxidizing agent. Using separate compartments, such a reaction can be used to generate electrons in an arrangement called a galvanic cell.

**Thermodynamics of Galvanic Cells** The voltage measured in a galvanic cell can be broken down into the electrode potentials of the anode (where oxidation takes place) and cathode (where reduction takes place). This voltage can be related to the Gibbs free energy change and the equilibrium constant of the redox process. The Nernst equation relates the cell voltage to the cell voltage under standard-state conditions and the concentrations of reacting species.

**Batteries** Batteries are electrochemical cells that can supply direct electric current at a constant voltage. There are many different types of batteries used in automobiles, flashlights, and pacemakers. Fuel cells are a special type of electrochemical cell that generates electricity by the oxidation of hydrogen or hydrocarbons.

**Corrosion** Corrosion is a spontaneous redox reaction that results in the formation of rust from iron, silver sulfide from silver, and patina (copper carbonate) from copper. Corrosion causes enormous damage to buildings, structures, ships, and cars. Many methods have been devised to prevent or minimize the effect of corrosion.

**Electrolysis** Electrolysis is the process in which electrical energy is used to cause a nonspontaneous redox reaction to occur. The quantitative relationship between the current supplied and the products formed is provided by Faraday. Electrolysis is the major method for producing active metals and nonmetals and many essential industrial chemicals.

## 19.1 Redox Reactions

**Electrochemistry** is the branch of chemistry that deals with the interconversion of electrical energy and chemical energy. Electrochemical processes are redox (oxidation-reduction) reactions in which the energy released by a spontaneous reaction is converted to electricity or in which electrical energy is used to cause a nonspontaneous reaction to occur. Although redox reactions were discussed in Chapter 4, it is helpful to review some of the basic concepts that will come up again in this chapter.

In redox reactions electrons are transferred from one substance to another. The reaction between magnesium metal and hydrochloric acid is an example of a redox reaction:



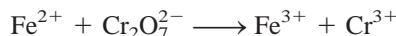
Recall that the numbers above the elements are the oxidation numbers of the elements. The loss of electrons by an element during oxidation is marked by an increase in the element's oxidation number. In reduction, there is a decrease in oxidation number resulting from a gain of electrons by an element. In the preceding reaction Mg metal is oxidized and  $\text{H}^+$  ions are reduced; the  $\text{Cl}^-$  ions are spectator ions.

### Balancing Redox Equations

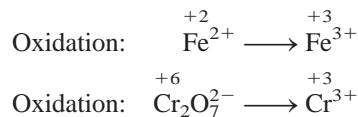
Equations for redox reactions like the preceding one are relatively easy to balance. However, in the laboratory we often encounter more complex redox reactions involving oxoanions such as chromate ( $\text{CrO}_4^{2-}$ ), dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ), permanganate ( $\text{MnO}_4^-$ ), nitrate ( $\text{NO}_3^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ). In principle, we can balance any redox equation using the procedure outlined in Section 3.7, but there are some special techniques for handling redox reactions, techniques that also give us insight into electron transfer processes. Here we will discuss one such procedure, called the *half-reaction method*. In this approach, the overall reaction is divided into two half-reactions, one for oxidation and one for reduction. The equations for the two half-reactions are balanced separately and then added together to give the overall balanced equation.

Suppose we are asked to balance the equation showing the oxidation of  $\text{Fe}^{2+}$  ions to  $\text{Fe}^{3+}$  ions by dichromate ions ( $\text{Cr}_2\text{O}_7^{2-}$ ) in an acidic medium. As a result, the  $\text{Cr}_2\text{O}_7^{2-}$  ions are reduced to  $\text{Cr}^{3+}$  ions. The following steps will help us balance the equation.

**Step 1:** Write the unbalanced equation for the reaction in ionic form.

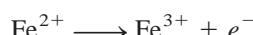


**Step 2:** Separate the equation into two half-reactions.



**Step 3:** Balance each half-reaction for number and type of atoms and charges. For reactions in an acidic medium, add  $\text{H}_2\text{O}$  to balance the O atoms and  $\text{H}^+$  to balance the H atoms.

Oxidation half-reaction: The atoms are already balanced. To balance the charge, we add an electron to the right-hand side of the arrow:



**Interactivity:**  
Redox Reactions—Oxidation States for Nitrogen  
ARIS, Interactives



**Interactivity:**  
Redox Reactions—Oxidized or Reduced?  
ARIS, Interactives

In an oxidation half-reaction, electrons appear as a product; in a reduction half-reaction, electrons appear as a reactant.

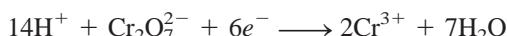
Reduction half-reaction: Because the reaction takes place in an acidic medium, we add seven H<sub>2</sub>O molecules to the right-hand side of the arrow to balance the O atoms:



To balance the H atoms, we add 14 H<sup>+</sup> ions on the left-hand side:

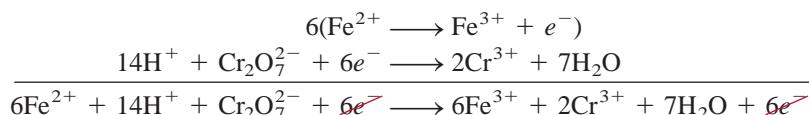


There are now 12 positive charges on the left-hand side and only six positive charges on the right-hand side. Therefore, we add six electrons on the left



**Step 4:** Add the two half-reactions together and balance the final equation by inspection. The electrons on both sides must cancel. If the oxidation and reduction half-reactions contain different numbers of electrons, we need to multiply one or both half-reactions to equalize the number of electrons.

Here we have only one electron for the oxidation half-reaction and six electrons for the reduction half-reaction, so we need to multiply the oxidation half-reaction by 6 and write



The electrons on both sides cancel, and we are left with the balanced net ionic equation:



**Step 5:** Verify that the equation contains the same type and numbers of atoms and the same charges on both sides of the equation.

A final check shows that the resulting equation is “atomically” and “electrically” balanced.

For reactions in a basic medium, we proceed through step 4 as if the reaction were carried out in an acidic medium. Then, for every H<sup>+</sup> ion we add an equal number of OH<sup>-</sup> ions to both sides of the equation. Where H<sup>+</sup> and OH<sup>-</sup> ions appear on the same side of the equation, we combine the ions to give H<sub>2</sub>O. Example 19.1 illustrates this procedure.

### Example 19.1

Write a balanced ionic equation to represent the oxidation of iodide ion (I<sup>-</sup>) by permanganate ion (MnO<sub>4</sub><sup>-</sup>) in basic solution to yield molecular iodine (I<sub>2</sub>) and manganese(IV) oxide (MnO<sub>2</sub>).

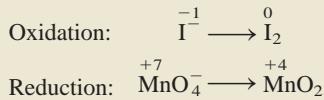
**Strategy** We follow the preceding procedure for balancing redox equations. Note that the reaction takes place in a basic medium.

**Solution** *Step 1:* The unbalanced equation is



(Continued)

*Step 2:* The two half-reactions are

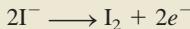


*Step 3:* We balance each half-reaction for number and type of atoms and charges.

Oxidation half-reaction: We first balance the I atoms:



To balance charges, we add two electrons to the right-hand side of the equation:



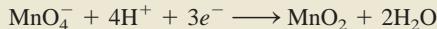
Reduction half-reaction: To balance the O atoms, we add two H<sub>2</sub>O molecules on the right:



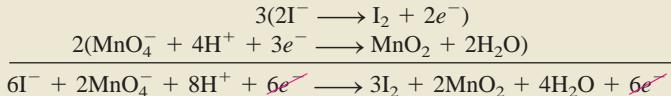
To balance the H atoms, we add four H<sup>+</sup> ions on the left:



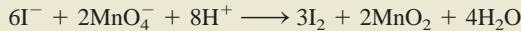
There are three net positive charges on the left, so we add three electrons to the same side to balance the charges:



*Step 4:* We now add the oxidation and reduction half reactions to give the overall reaction. To equalize the number of electrons, we need to multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2 as follows:



The electrons on both sides cancel, and we are left with the balanced net ionic equation:



This is the balanced equation in an acidic medium. However, because the reaction is carried out in a basic medium, for every H<sup>+</sup> ion we need to add an equal number of OH<sup>-</sup> ions to both sides of the equation:



Finally, combining the H<sup>+</sup> and OH<sup>-</sup> ions to form water, we obtain



To carry out this reaction, mix KI and KMnO<sub>4</sub> in a basic medium.

*Step 5:* A final check shows that the equation is balanced in terms of both atoms and charges.

Similar problems: 19.1, 19.2.

**Practice Exercise** Balance the following equation for the reaction in an acidic medium by the half-reaction method:



## 19.2 Galvanic Cells

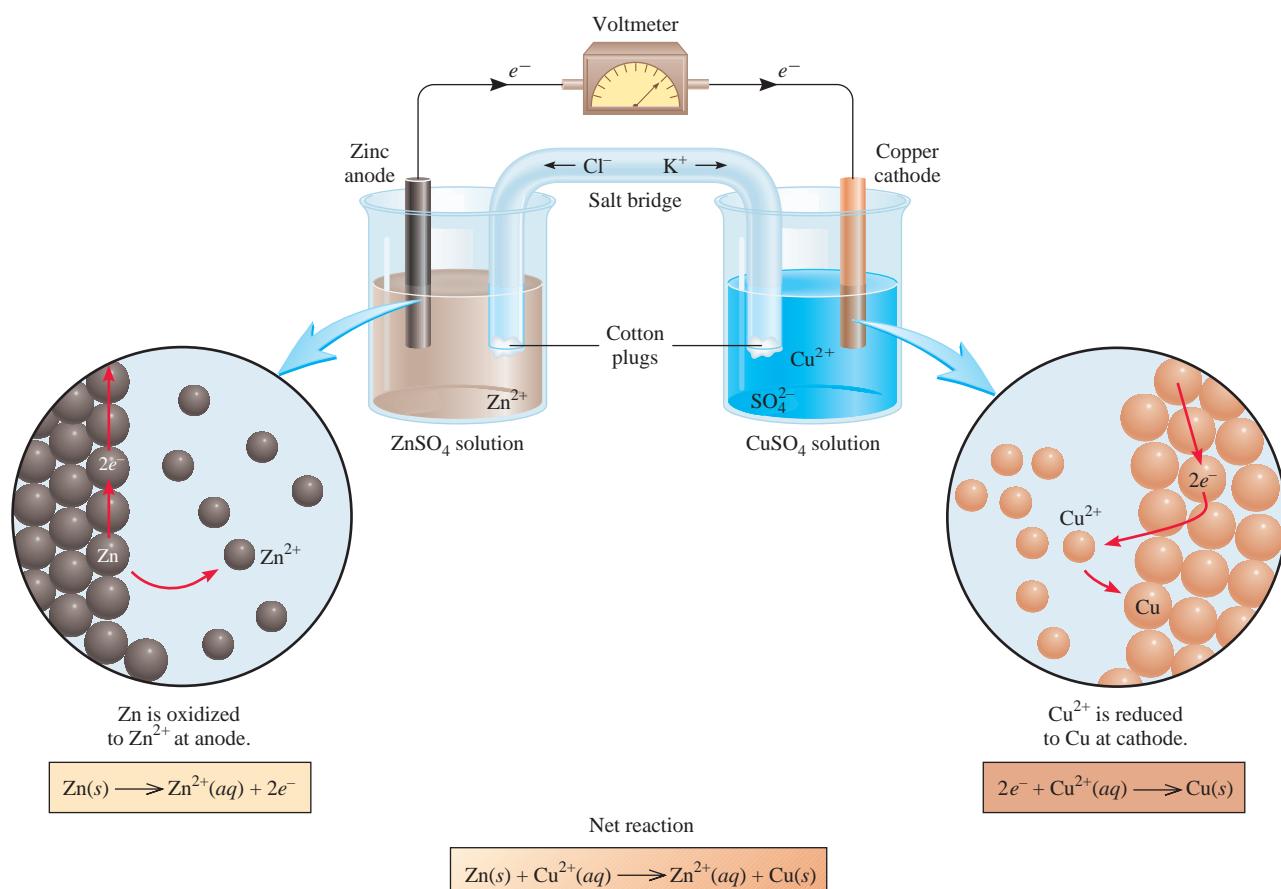
In Section 4.4 we saw that when a piece of zinc metal is placed in a  $\text{CuSO}_4$  solution, Zn is oxidized to  $\text{Zn}^{2+}$  ions while  $\text{Cu}^{2+}$  ions are reduced to metallic copper (see Figure 4.13):



The electrons are transferred directly from the reducing agent (Zn) to the oxidizing agent ( $\text{Cu}^{2+}$ ) in solution. However, if we physically separate the oxidizing agent from the reducing agent, the transfer of electrons can take place via an external conducting medium (a metal wire). As the reaction progresses, it sets up a constant flow of electrons and hence generates electricity (that is, it produces electrical work such as driving an electric motor).



The experimental apparatus for generating electricity through the use of a spontaneous reaction is called a **galvanic cell** or **voltaic cell**, after the Italian scientists Luigi Galvani and Alessandro Volta, who constructed early versions of the device. Figure 19.1 shows the essential components of a galvanic cell. A zinc bar is immersed



**Figure 19.1**

A galvanic cell. The salt bridge (an inverted U tube) containing a  $\text{KCl}$  solution provides an electrically conducting medium between two solutions. The openings of the U tube are loosely plugged with cotton balls to prevent the  $\text{KCl}$  solution from flowing into the containers while allowing the anions and cations to move across. Electrons flow externally from the Zn electrode (anode) to the Cu electrode (cathode).

in a  $\text{ZnSO}_4$  solution, and a copper bar is immersed in a  $\text{CuSO}_4$  solution. The cell operates on the principle that the oxidation of Zn to  $\text{Zn}^{2+}$  and the reduction of  $\text{Cu}^{2+}$  to Cu can be made to take place simultaneously in separate locations with the transfer of electrons between them occurring through an external wire. The zinc and copper bars are called *electrodes*. This particular arrangement of electrodes (Zn and Cu) and solutions ( $\text{ZnSO}_4$  and  $\text{CuSO}_4$ ) is called the Daniell cell. By definition, the *anode* in a galvanic cell is *the electrode at which oxidation occurs* and the *cathode* is *the electrode at which reduction occurs*.

For the Daniell cell, the *half-cell reactions*, that is, *the oxidation and reduction reactions at the electrodes*, are



Alphabetically anode precedes cathode  
and oxidation precedes reduction.  
Therefore, anode is where oxidation  
occurs and cathode is where reduction  
takes place.

Half-cell reactions are similar to the half-reactions discussed earlier.

Note that unless the two solutions are separated from each other, the  $\text{Cu}^{2+}$  ions will react directly with the zinc bar:



and no useful electrical work will be obtained.

To complete the electrical circuit, the solutions must be connected by a conducting medium through which the cations and anions can move from one electrode compartment to the other. This requirement is satisfied by a *salt bridge*, which, in its simplest form, is an inverted U tube containing an inert electrolyte solution, such as KCl or  $\text{NH}_4\text{NO}_3$ , whose ions will not react with other ions in solution or with the electrodes (see Figure 19.1). During the course of the overall redox reaction, electrons flow externally from the anode (Zn electrode) through the wire and voltmeter to the cathode (Cu electrode). In the solution, the cations ( $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{K}^+$ ) move toward the cathode, while the anions ( $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) move toward the anode. Without the salt bridge connecting the two solutions, the buildup of positive charge in the anode compartment (due to the formation of  $\text{Zn}^{2+}$  ions) and negative charge in the cathode compartment (created when some of the  $\text{Cu}^{2+}$  ions are reduced to Cu) would quickly prevent the cell from operating.

An electric current flows from the anode to the cathode because there is a difference in electrical potential energy between the electrodes. This flow of electric current is analogous to that of water down a waterfall, which occurs because there is a difference in gravitational potential energy, or the flow of gas from a high-pressure region to a low-pressure region. The voltage across the electrodes of a galvanic cell is called the *cell voltage*, or *cell potential*. Experimentally, this is measured by a voltmeter (Figure 19.2). Another common term for the cell potential is the *electromotive force* or *emf* (*E*), which, despite the name, is a measure of voltage, not force. We will see that the voltage of a cell depends not only on the nature of electrodes and the ions, but also on the concentrations of the ions and the temperature at which the cell is operated.

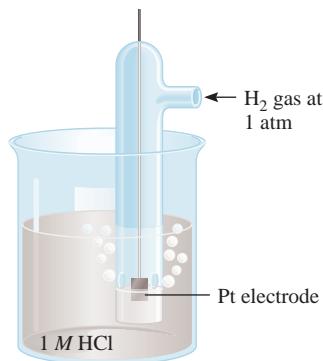
The conventional notation for representing galvanic cells is the *cell diagram*. For the Daniell cell shown in Figure 19.1, if we assume that the concentrations of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ions are 1 M, the cell diagram is



The single vertical line represents a phase boundary. For example, the zinc electrode is a solid and the  $\text{Zn}^{2+}$  ions (from  $\text{ZnSO}_4$ ) are in solution. Thus, we draw a line between Zn and  $\text{Zn}^{2+}$  to show the phase boundary. The double vertical lines denote

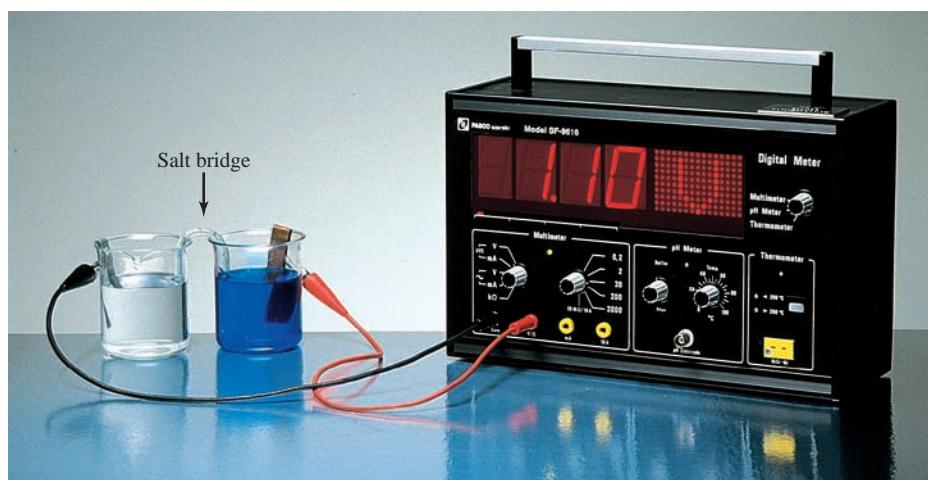
**Figure 19.2**

Practical setup of the galvanic cell described in Figure 19.1. Note the U tube (salt bridge) connecting the two beakers. When the concentrations of  $ZnSO_4$  and  $CuSO_4$  are 1 molar (1 M) at  $25^\circ C$ , the cell voltage is 1.10 V.

**Figure 19.3**

A hydrogen electrode operating under standard-state conditions. Hydrogen gas at 1 atm is bubbled through a 1 M HCl solution. The platinum electrode is part of the hydrogen electrode.

The choice of an arbitrary reference for measuring electrode potential is analogous to choosing the surface of the ocean as the reference for altitude, calling it zero meters, and then referring to any terrestrial altitude as being a certain number of meters above or below sea level.



the salt bridge. By convention, the anode is written first, to the left of the double lines and the other components appear in the order in which we would encounter them in moving from the anode to the cathode.

### 19.3 Standard Reduction Potentials

When the concentrations of the  $Cu^{2+}$  and  $Zn^{2+}$  ions are both 1.0 M, we find that the voltage or emf of the Daniell cell is 1.10 V at  $25^\circ C$  (see Figure 19.2). This voltage must be related directly to the redox reactions, but how? Just as the overall cell reaction can be thought of as the sum of two half-cell reactions, the measured emf of the cell can be treated as the sum of the electrical potentials at the Zn and Cu electrodes. Knowing one of these electrode potentials, we could obtain the other by subtraction (from 1.10 V). It is impossible to measure the potential of just a single electrode, but if we arbitrarily set the potential value of a particular electrode at zero, we can use it to determine the relative potentials of other electrodes. The hydrogen electrode, shown in Figure 19.3, serves as the reference for this purpose. Hydrogen gas is bubbled into a hydrochloric acid solution at  $25^\circ C$ . The platinum electrode has two functions. First, it provides a surface on which the dissociation of hydrogen molecules can take place:



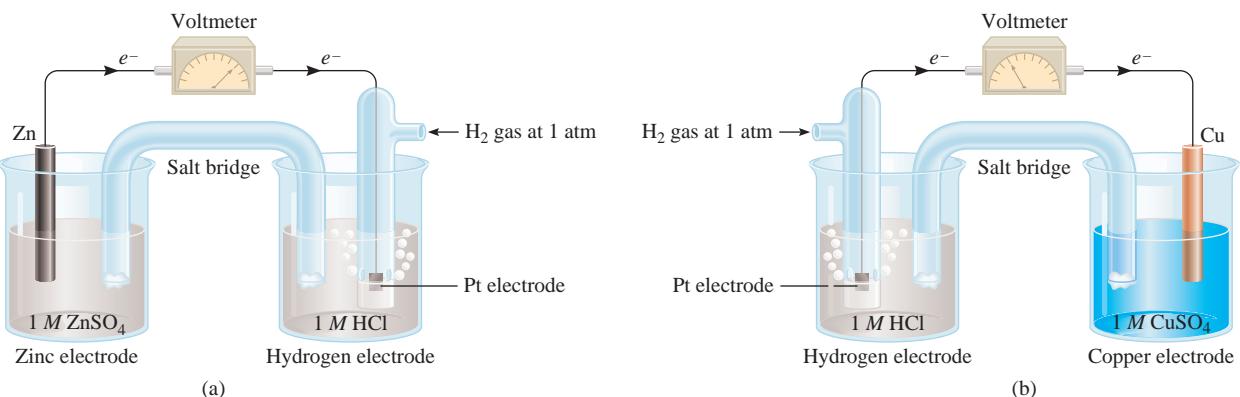
Second, it serves as an electrical conductor to the external circuit.

Under standard-state conditions (when the pressure of  $H_2$  is 1 atm and the concentration of the HCl solution is 1 M; see Table 18.2), the potential for the reduction of  $H^+$  at  $25^\circ C$  is taken to be *exactly* zero:



The superscript “ $^\circ$ ” denotes standard-state conditions, and  $E^\circ$  is the **standard reduction potential**, or the voltage associated with a reduction reaction at an electrode when all solutes are 1 M and all gases are at 1 atm. Thus, the standard reduction potential of the hydrogen electrode is defined as zero. The hydrogen electrode is called the **standard hydrogen electrode (SHE)**.

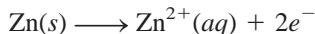
Standard states are defined in Table 18.2 (p. 624).



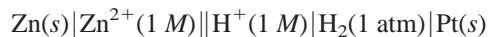
**Figure 19.4**

(a) A cell consisting of a zinc electrode and a hydrogen electrode. (b) A cell consisting of a copper electrode and a hydrogen electrode. Both cells are operating under standard-state conditions. Note that in (a) the SHE acts as the cathode, but in (b) it is the anode.

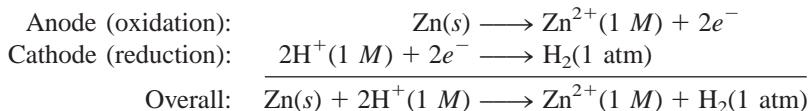
We can use the SHE to measure the potentials of other kinds of electrodes. For example, Figure 19.4(a) shows a galvanic cell with a zinc electrode and a SHE. In this case the zinc electrode is the anode and the SHE is the cathode. We deduce this fact from the decrease in mass of the zinc electrode during the operation of the cell, which is consistent with the loss of zinc to the solution caused by the oxidation reaction:



The cell diagram is



As mentioned earlier, the Pt electrode provides the surface on which the reduction takes place. When all the reactants are in their standard states (that is, H<sub>2</sub> at 1 atm, H<sup>+</sup> and Zn<sup>2+</sup> ions at 1 M), the emf of the cell is 0.76 V at 25°C. We can write the half-cell reactions as follows:



By convention, the ***standard emf*** of the cell,  $E_{cell}^\circ$ , which is composed of a contribution from the anode and a contribution from the cathode, is given by

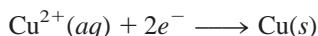
$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \quad (19.1)$$

where both  $E_{\text{cathode}}^\circ$  and  $E_{\text{anode}}^\circ$  are the standard reduction potentials of the electrodes. For the Zn-SHE cell, we write

$$E_{\text{cell}}^{\circ} = E_{\text{H}^{+}/\text{H}_2}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

where the subscript  $H^+/H_2$  means  $2H^+ + 2e^- \rightarrow H_2$  and the subscript  $Zn^{2+}/Zn$  means  $Zn^{2+} + 2e^- \rightarrow Zn$ . Thus, the standard reduction potential of zinc,  $E_{Zn^{2+}/Zn}^\circ$ , is  $-0.76\text{ V}$ .

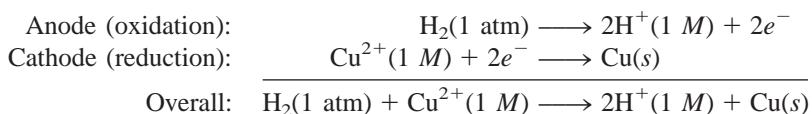
The standard electrode potential of copper can be obtained in a similar fashion, by using a cell with a copper electrode and a SHE [Figure 19.4(b)]. In this case, the copper electrode is the cathode because its mass increases during the operation of the cell, as is consistent with the reduction reaction:



The cell diagram is



and the half-cell reactions are

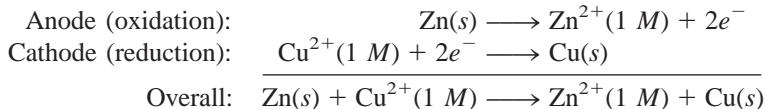


Under standard-state conditions and at 25°C, the emf of the cell is 0.34 V, so we write

$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \\ 0.34 \text{ V} &= E_{\text{Cu}^{2+}/\text{Cu}}^\circ - E_{\text{H}^+/\text{H}_2}^\circ \\ &= E_{\text{Cu}^{2+}/\text{Cu}}^\circ - 0 \end{aligned}$$

In this case, the standard reduction potential of copper,  $E_{\text{Cu}^{2+}/\text{Cu}}^\circ$ , is 0.34 V, where the subscript means  $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ .

For the Daniell cell shown in Figure 19.1, we can now write



The emf of the cell is

$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \\ &= E_{\text{Cu}^{2+}/\text{Cu}}^\circ - E_{\text{Zn}^{2+}/\text{Zn}}^\circ \\ &= 0.34 \text{ V} - (-0.76 \text{ V}) \\ &= 1.10 \text{ V} \end{aligned}$$

As in the case of  $\Delta G^\circ$  (p. 630), we can use the sign of  $E^\circ$  to predict the extent of a redox reaction. A positive  $E^\circ$  means the redox reaction will favor the formation of products at equilibrium. Conversely, a negative  $E^\circ$  means that more reactants than products will be formed at equilibrium. We will examine the relationships among  $E_{\text{cell}}^\circ$ ,  $\Delta G^\circ$ , and  $K$  later in this chapter.

The activity series in Figure 4.14 is based on data given in Table 19.1.

Table 19.1 lists standard reduction potentials for a number of half-cell reactions. By definition, the SHE has an  $E^\circ$  value of 0.00 V. Below the SHE the negative standard reduction potentials increase, and above it the positive standard reduction potentials increase. It is important to know the following points about the table in calculations:

1. The  $E^\circ$  values apply to the half-cell reactions as read in the forward (left to right) direction.
2. The more positive  $E^\circ$  is, the greater the tendency for the substance to be reduced. For example, the half-cell reaction



**TABLE 19.1** Standard Reduction Potentials at 25°C\*

| Half-Reaction  | $E^\circ$ (V) |
|--|---------------|
| $\text{F}_2(g) + 2e^- \longrightarrow 2\text{F}^-(aq)$   | +2.87         |
| $\text{O}_3(g) + 2\text{H}^+(aq) + 2e^- \longrightarrow \text{O}_2(g) + \text{H}_2\text{O}$                              | +2.07         |
| $\text{Co}^{3+}(aq) + e^- \longrightarrow \text{Co}^{2+}(aq)$  | +1.82         |
| $\text{H}_2\text{O}_2(aq) + 2\text{H}^+(aq) + 2e^- \longrightarrow 2\text{H}_2\text{O}$                                  | +1.77         |
| $\text{PbO}_2(s) + 4\text{H}^+(aq) + \text{SO}_4^{2-}(aq) + 2e^- \longrightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}$ | +1.70         |
| $\text{Ce}^{4+}(aq) + e^- \longrightarrow \text{Ce}^{3+}(aq)$  | +1.61         |
| $\text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5e^- \longrightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}$                   | +1.51         |
| $\text{Au}^{3+}(aq) + 3e^- \longrightarrow \text{Au}(s)$   | +1.50         |
| $\text{Cl}_2(g) + 2e^- \longrightarrow 2\text{Cl}^-(aq)$   | +1.36         |
| $\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6e^- \longrightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}$     | +1.33         |
| $\text{MnO}_2(s) + 4\text{H}^+(aq) + 2e^- \longrightarrow \text{Mn}^{2+}(aq) + 2\text{H}_2\text{O}$                      | +1.23         |
| $\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \longrightarrow 2\text{H}_2\text{O}$   | +1.23         |
| $\text{Br}_2(l) + 2e^- \longrightarrow 2\text{Br}^-(aq)$   | +1.07         |
| $\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \longrightarrow \text{NO}(g) + 2\text{H}_2\text{O}$                          | +0.96         |
| $2\text{Hg}^{2+}(aq) + 2e^- \longrightarrow \text{Hg}_2^{2+}(aq)$  | +0.92         |
| $\text{Hg}_2^{2+}(aq) + 2e^- \longrightarrow 2\text{Hg}(l)$  | +0.85         |
| $\text{Ag}^+(aq) + e^- \longrightarrow \text{Ag}(s)$   | +0.80         |
| $\text{Fe}^{3+}(aq) + e^- \longrightarrow \text{Fe}^{2+}(aq)$  | +0.77         |
| $\text{O}_2(g) + 2\text{H}^+(aq) + 2e^- \longrightarrow \text{H}_2\text{O}_2(aq)$  | +0.68         |
| $\text{MnO}_4^-(aq) + 2\text{H}_2\text{O} + 3e^- \longrightarrow \text{MnO}_2(s) + 4\text{OH}^-(aq)$                     | +0.59         |
| $\text{I}_2(s) + 2e^- \longrightarrow 2\text{I}^-(aq)$   | +0.53         |
| $\text{O}_2(g) + 2\text{H}_2\text{O} + 4e^- \longrightarrow 4\text{OH}^-(aq)$  | +0.40         |
| $\text{Cu}^{2+}(aq) + 2e^- \longrightarrow \text{Cu}(s)$   | +0.34         |
| $\text{AgCl}(s) + e^- \longrightarrow \text{Ag}(s) + \text{Cl}^-(aq)$  | +0.22         |
| $\text{SO}_4^{2-}(aq) + 4\text{H}^+(aq) + 2e^- \longrightarrow \text{SO}_2(g) + 2\text{H}_2\text{O}$                     | +0.20         |
| $\text{Cu}^{2+}(aq) + e^- \longrightarrow \text{Cu}^+(aq)$   | +0.15         |
| $\text{Sn}^{4+}(aq) + 2e^- \longrightarrow \text{Sn}^{2+}(aq)$   | +0.13         |
| $2\text{H}^+(aq) + 2e^- \longrightarrow \text{H}_2(g)$   | 0.00          |
| $\text{Pb}^{2+}(aq) + 2e^- \longrightarrow \text{Pb}(s)$   | -0.13         |
| $\text{Sn}^{2+}(aq) + 2e^- \longrightarrow \text{Sn}(s)$   | -0.14         |
| $\text{Ni}^{2+}(aq) + 2e^- \longrightarrow \text{Ni}(s)$   | -0.25         |
| $\text{Co}^{2+}(aq) + 2e^- \longrightarrow \text{Co}(s)$   | -0.28         |
| $\text{PbSO}_4(s) + 2e^- \longrightarrow \text{Pb}(s) + \text{SO}_4^{2-}(aq)$  | -0.31         |
| $\text{Cd}^{2+}(aq) + 2e^- \longrightarrow \text{Cd}(s)$   | -0.40         |
| $\text{Fe}^{2+}(aq) + 2e^- \longrightarrow \text{Fe}(s)$   | -0.44         |
| $\text{Cr}^{3+}(aq) + 3e^- \longrightarrow \text{Cr}(s)$   | -0.74         |
| $\text{Zn}^{2+}(aq) + 2e^- \longrightarrow \text{Zn}(s)$   | -0.76         |
| $2\text{H}_2\text{O} + 2e^- \longrightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$  | -0.83         |
| $\text{Mn}^{2+}(aq) + 2e^- \longrightarrow \text{Mn}(s)$   | -1.18         |
| $\text{Al}^{3+}(aq) + 3e^- \longrightarrow \text{Al}(s)$   | -1.66         |
| $\text{Be}^{2+}(aq) + 2e^- \longrightarrow \text{Be}(s)$   | -1.85         |
| $\text{Mg}^{2+}(aq) + 2e^- \longrightarrow \text{Mg}(s)$   | -2.37         |
| $\text{Na}^+(aq) + e^- \longrightarrow \text{Na}(s)$   | -2.71         |
| $\text{Ca}^{2+}(aq) + 2e^- \longrightarrow \text{Ca}(s)$   | -2.87         |
| $\text{Sr}^{2+}(aq) + 2e^- \longrightarrow \text{Sr}(s)$   | -2.89         |
| $\text{Ba}^{2+}(aq) + 2e^- \longrightarrow \text{Ba}(s)$   | -2.90         |
| $\text{K}^+(aq) + e^- \longrightarrow \text{K}(s)$   | -2.93         |
| $\text{Li}^+(aq) + e^- \longrightarrow \text{Li}(s)$   | -3.05         |

Increasing strength as oxidizing agent ↑

↓ Increasing strength as reducing agent

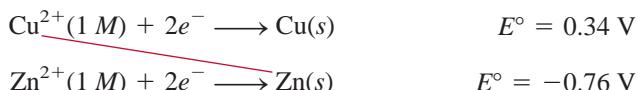
\*For all half-reactions the concentration is 1 M for dissolved species and the pressure is 1 atm for gases. These are the standard-state values.

has the highest positive  $E^\circ$  value among all the half-cell reactions. Thus,  $\text{F}_2$  is the *strongest* oxidizing agent because it has the greatest tendency to be reduced. At the other extreme is the reaction



which has the most negative  $E^\circ$  value. Thus,  $\text{Li}^+$  is the *weakest* oxidizing agent because it is the most difficult species to reduce. Conversely, we say that  $\text{F}^-$  is the weakest reducing agent and Li metal is the strongest reducing agent. Under standard-state conditions, the oxidizing agents (the species on the left-hand side of the half-reactions in Table 19.1) increase in strength from bottom to top and the reducing agents (the species on the right-hand side of the half-reactions) increase in strength from top to bottom.

3. The half-cell reactions are reversible. Depending on the conditions, any electrode can act either as an anode or as a cathode. Earlier we saw that the SHE is the cathode ( $\text{H}^+$  is reduced to  $\text{H}_2$ ) when coupled with zinc in a cell and that it becomes the anode ( $\text{H}_2$  is oxidized to  $\text{H}^+$ ) when used in a cell with copper.
4. Under standard-state conditions, any species on the left of a given half-cell reaction will react spontaneously with a species that appears on the right of any half-cell reaction located *below* it in Table 19.1. This principle is sometimes called the *diagonal rule*. In the case of the Daniell cell,



We see that the substance on the left of the first half-cell reaction is  $\text{Cu}^{2+}$  and the substance on the right in the second half-cell reaction is Zn. Therefore, as we saw earlier, Zn spontaneously reduces  $\text{Cu}^{2+}$  to form  $\text{Zn}^{2+}$  and Cu.

5. Changing the stoichiometric coefficients of a half-cell reaction *does not* affect the value of  $E^\circ$  because electrode potentials are intensive properties. This means that the value of  $E^\circ$  is unaffected by the size of the electrodes or the amount of solutions present. For example,



but  $E^\circ$  does not change if we multiply the half-reaction by 2:



6. Like  $\Delta H$ ,  $\Delta G$ , and  $\Delta S$ , the sign of  $E^\circ$  changes but its magnitude remains the same when we reverse a reaction.

As Examples 19.2 and 19.3 show, Table 19.1 enables us to predict the outcome of redox reactions under standard-state conditions, whether they take place in a galvanic cell, where the reducing agent and oxidizing agent are physically separated from each other, or in a beaker, where the reactants are all mixed together.

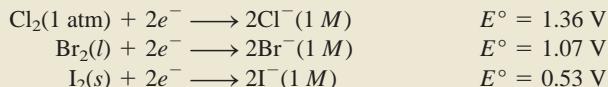
### Example 19.2

Predict what will happen if molecular bromine ( $\text{Br}_2$ ) is added to a solution containing NaCl and NaI at 25°C. Assume all species are in their standard states.

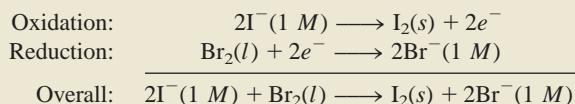
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**Strategy** To predict what redox reaction(s) will take place, we need to compare the standard reduction potentials of  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$  and apply the diagonal rule.

**Solution** From Table 19.1, we write the standard reduction potentials as follows:



Applying the diagonal rule we see that  $\text{Br}_2$  will oxidize  $\text{I}^-$  but will not oxidize  $\text{Cl}^-$ . Therefore, the only redox reaction that will occur appreciably under standard-state conditions is



**Check** We can confirm our conclusion by calculating  $E_{\text{cell}}^\circ$ . Try it. Note that the  $\text{Na}^+$  ions are inert and do not enter into the redox reaction.

Similar problems: 19.14, 19.17.

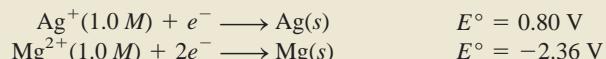
**Practice Exercise** Can Sn reduce  $\text{Zn}^{2+}(aq)$  under standard-state conditions?

### Example 19.3

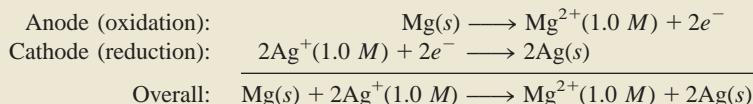
A galvanic cell consists of a Mg electrode in a 1.0 M  $\text{Mg}(\text{NO}_3)_2$  solution and a Ag electrode in a 1.0 M  $\text{AgNO}_3$  solution. Calculate the standard emf of this cell at 25°C.

**Strategy** At first it may not be clear how to assign the electrodes in the galvanic cell. From Table 19.1 we write the standard reduction potentials of Ag and Mg and apply the diagonal rule to determine which is the anode and which is the cathode.

**Solution** The standard reduction potentials are



Applying the diagonal rule, we see that  $\text{Ag}^+$  will oxidize Mg:



Note that in order to balance the overall equation we multiplied the reduction of  $\text{Ag}^+$  by 2. We can do so because, as an intensive property,  $E^\circ$  is not affected by this procedure. We find the emf of the cell by using Equation (19.1) and Table 19.1:

$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \\ &= E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Mg}^{2+}/\text{Mg}}^\circ \\ &= 0.80 \text{ V} - (-2.37 \text{ V}) \\ &= 3.17 \text{ V} \end{aligned}$$

**Check** The positive value of  $E^\circ$  shows that the forward reaction is favored.

Similar problems: 19.11, 19.12.

**Practice Exercise** What is the standard emf of a galvanic cell made of a Cd electrode in a 1.0 M  $\text{Cd}(\text{NO}_3)_2$  solution and a Cr electrode in a 1.0 M  $\text{Cr}(\text{NO}_3)_3$  solution at 25°C?

## 19.4 Thermodynamics of Redox Reactions

Our next step is to see how  $E_{\text{cell}}^{\circ}$  is related to thermodynamic quantities such as  $\Delta G^{\circ}$  and  $K$ . In a galvanic cell, chemical energy is converted to electrical energy to do electrical work. Electrical energy in this case is the product of the emf of the cell and the total electrical charge (in coulombs) that passes through the cell:

$$1 \text{ J} = 1 \text{ V} \times 1 \text{ C}$$

$$\begin{aligned}\text{electrical energy} &= \text{volts} \times \text{coulombs} \\ &= \text{joules}\end{aligned}$$

The total charge is determined by the number of electrons that pass through the cell, so we have

$$\text{total charge} = \text{number of } e^- \times \text{charge of one } e^-$$

In general, it is more convenient to express the total charge in molar quantities. The charge of one mole of electrons is called the **Faraday constant ( $F$ )**, after the English chemist and physicist Michael Faraday, where

**In most calculations, we round the Faraday constant to 96,500 C/mol  $e^-$ .**

$$\begin{aligned}1 \text{ F} &= 6.022 \times 10^{23} \text{ } e^-/\text{mol } e^- \times 1.602 \times 10^{-19} \text{ C}/e^- \\ &= 9.647 \times 10^4 \text{ C/mol } e^-\end{aligned}$$

Therefore, the total charge can now be expressed as  $nF$ , where  $n$  is the number of moles of electrons exchanged between the reducing agent and the oxidizing agent in the overall redox equation.

The measured emf ( $E_{\text{cell}}$ ) is the *maximum* voltage the cell can achieve. It is given by the electrical work done ( $w_{\text{ele}}$ ) divided by the total charge; that is,

$$E_{\text{cell}} = \frac{-w_{\text{ele}}}{\text{total charge}} = \frac{-w_{\text{ele}}}{nF}$$

or

$$w_{\text{ele}} = -nFE_{\text{cell}}$$

**The sign convention for electrical work is the same as that for P-V work, discussed in Section 6.3.**

The negative sign indicates that the electrical work is done by the system (galvanic cell) on the surroundings. In Chapter 18 we defined free energy as the energy available to do work. Specifically, the change in free energy ( $\Delta G$ ) represents the maximum amount of useful work that can be obtained in a reaction:

$$\Delta G = w_{\text{max}} = w_{\text{ele}}$$

Therefore, we can write

$$\Delta G = -nFE_{\text{cell}} \quad (19.2)$$

Both  $n$  and  $F$  are positive quantities and  $\Delta G$  is negative for a spontaneous process, so  $E_{\text{cell}}$  must be positive. For reactions in which reactants and products are in their standard states, Equation (19.2) becomes

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} \quad (19.3)$$

Now we can relate  $E_{\text{cell}}^{\circ}$  to the equilibrium constant ( $K$ ) of a redox reaction. In Section 18.5 we saw that the standard free-energy change  $\Delta G^{\circ}$  for a reaction is related to its equilibrium constant as follows [see Equation (18.14)]:

$$\Delta G^{\circ} = -RT \ln K$$

Therefore, if we combine Equations (18.14) and (19.3) we obtain

$$-nFE_{\text{cell}}^{\circ} = -RT \ln K$$

Solving for  $E_{\text{cell}}^{\circ}$

$$E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln K \quad (19.4)$$

When  $T = 298$  K, Equation (19.4) can be simplified by substituting for  $R$  and  $F$ :

$$E_{\text{cell}}^{\circ} = \frac{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}{n(96,500 \text{ J/V} \cdot \text{mol})} \ln K$$

In calculations involving  $F$ , we sometimes omit the symbol  $e^-$ .

$$E_{\text{cell}}^{\circ} = \frac{0.0257 \text{ V}}{n} \ln K \quad (19.5)$$

Alternatively, Equation (19.5) can be written using the base-10 logarithm of  $K$ :

$$E_{\text{cell}}^{\circ} = \frac{0.0592 \text{ V}}{n} \log K \quad (19.6)$$

Thus, if any one of the three quantities  $\Delta G^\circ$ ,  $K$ , or  $E_{\text{cell}}^{\circ}$  is known, the other two can be calculated using Equation (18.14), Equation (19.3), or Equation (19.4) (Figure 19.5). We summarize the relationships among  $\Delta G^\circ$ ,  $K$ , and  $E_{\text{cell}}^{\circ}$  and characterize the spontaneity of a redox reaction in Table 19.2. For simplicity, we will omit the subscript “cell” in  $E^\circ$  and  $E$ .

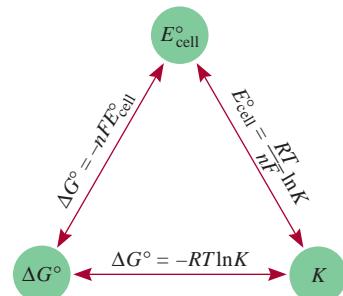
### Example 19.4

Calculate the equilibrium constant for the following reaction at 25°C:



**Strategy** The relationship between the equilibrium constant  $K$  and the standard emf is given by Equation (19.5):  $E_{\text{cell}}^{\circ} = (0.0257 \text{ V}/n)\ln K$ . Thus, if we can determine the standard emf, we can calculate the equilibrium constant. We can determine the  $E_{\text{cell}}^{\circ}$  of a hypothetical galvanic cell made up of two couples ( $\text{Sn}^{2+}/\text{Sn}$  and  $\text{Cu}^{2+}/\text{Cu}^+$ ) from the standard reduction potentials in Table 19.1.

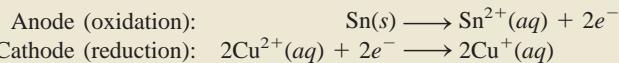
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**Figure 19.5**  
Relationships among  $E_{\text{cell}}^{\circ}$ ,  $K$ , and  $\Delta G^\circ$ .

| TABLE 19.2 Relationships Among $\Delta G^\circ$ , $K$ , and $E_{\text{cell}}^{\circ}$ |      |                           |   |
|---|------|---------------------------|---|
| $\Delta G^\circ$  | $K$  | $E_{\text{cell}}^{\circ}$ | Reaction Under Standard-State Conditions    |
| Negative  | $>1$ | Positive                  | Favors formation of products.               |
| 0   | $=1$ | 0                         | Reactants and products are equally favored. |
| Positive  | $<1$ | Negative                  | Favors formation of reactants.              |

**Solution** The half-cell reactions are



$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \\ &= E_{\text{Cu}^{2+}/\text{Cu}^+}^\circ - E_{\text{Sn}^{2+}/\text{Sn}}^\circ \\ &= 0.15 \text{ V} - (-0.14 \text{ V}) \\ &= 0.29 \text{ V} \end{aligned}$$

Equation (19.5) can be written

$$\ln K = \frac{nE^\circ}{0.0257 \text{ V}}$$

In the overall reaction we find  $n = 2$ . Therefore,

$$\begin{aligned} \ln K &= \frac{(2)(0.29 \text{ V})}{0.0257 \text{ V}} = 22.6 \\ K &= e^{22.6} = 7 \times 10^9 \end{aligned}$$

**Similar problems:** 19.21, 19.22.

**Practice Exercise** Calculate the equilibrium constant for the following reaction at 25°C:



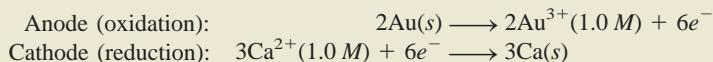
### Example 19.5

Calculate the standard free-energy change for the following reaction at 25°C:



**Strategy** The relationship between the standard free energy change and the standard emf of the cell is given by Equation (19.3):  $\Delta G^\circ = -nFE_{\text{cell}}^\circ$ . Thus, if we can determine  $E_{\text{cell}}^\circ$ , we can calculate  $\Delta G^\circ$ . We can determine the  $E_{\text{cell}}^\circ$  of a hypothetical galvanic cell made up of two couples ( $\text{Au}^{3+}/\text{Au}$  and  $\text{Ca}^{2+}/\text{Ca}$ ) from the standard reduction potentials in Table 19.1.

**Solution** The half-cell reactions are



$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \\ &= E_{\text{Ca}^{2+}/\text{Ca}}^\circ - E_{\text{Au}^{3+}/\text{Au}}^\circ \\ &= -2.87 \text{ V} - 1.50 \text{ V} \\ &= -4.37 \text{ V} \end{aligned}$$

Now we use Equation (19.3):

$$\Delta G^\circ = -nFE^\circ$$

The overall reaction shows that  $n = 6$ , so

$$\begin{aligned} \Delta G^\circ &= -(6)(96,500 \text{ J/V} \cdot \text{mol})(-4.37 \text{ V}) \\ &= 2.53 \times 10^6 \text{ J/mol} \\ &= 2.53 \times 10^3 \text{ kJ/mol} \end{aligned}$$

(Continued)

**Check** The large positive value of  $\Delta G^\circ$  tells us that the reaction favors the reactants at equilibrium. The result is consistent with the fact that  $E^\circ$  for the galvanic cell is negative.

**Similar problem:** 19.24.

**Practice Exercise** Calculate  $\Delta G^\circ$  for the following reaction at 25°C:



## 19.5 The Effect of Concentration on Cell Emf

So far we have focused on redox reactions in which reactants and products are in their standard states, but standard-state conditions are often difficult, and sometimes impossible, to maintain. Nevertheless, there is a mathematical relationship between the emf of a galvanic cell and the concentration of reactants and products in a redox reaction under nonstandard-state conditions. This equation is derived next.

### The Nernst Equation

Consider a redox reaction of the type



From Equation (18.13)

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Because  $\Delta G = -nFE$  and  $\Delta G^\circ = -nFE^\circ$ , the equation can be expressed as

$$-nFE = -nFE^\circ + RT \ln Q$$

Dividing the equation through by  $-nF$ , we get

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad (19.7)$$

where  $Q$  is the reaction quotient (see Section 15.3). Equation (19.7) is known as the **Nernst equation** (after the German chemist Walter Nernst). At 298 K, Equation (19.7) can be rewritten as

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q \quad (19.8)$$

or, expressing Equation (19.8) using the base-10 logarithm of  $Q$ :

$$E = E^\circ - \frac{0.0592 \text{ V}}{n} \log Q \quad (19.9)$$

During the operation of a galvanic cell, electrons flow from the anode to the cathode, resulting in product formation and a decrease in reactant concentration. Thus,  $Q$  increases, which means that  $E$  decreases. Eventually, the cell reaches equilibrium. At equilibrium, there is no net transfer of electrons, so  $E = 0$  and  $Q = K$ , where  $K$  is the equilibrium constant.

The Nernst equation enables us to calculate  $E$  as a function of reactant and product concentrations in a redox reaction. For example, for the Daniell cell in Figure 19.1,



The Nernst equation for this cell at 25°C can be written as

**Remember that concentrations of pure solids (and pure liquids) do not appear in the expression for  $Q$  (see p. 505).**

$$E = 1.10 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

If the ratio  $[\text{Zn}^{2+}]/[\text{Cu}^{2+}]$  is less than 1,  $\ln([\text{Zn}^{2+}]/[\text{Cu}^{2+}])$  is a negative number, so that the second term on the right-hand side of the preceding equation is positive. Under this condition  $E$  is greater than the standard emf  $E^\circ$ . If the ratio is greater than 1,  $E$  is smaller than  $E^\circ$ .

### Example 19.6

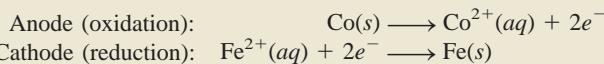
Predict whether the following reaction would proceed spontaneously as written at 298 K:



given that  $[\text{Co}^{2+}] = 0.15 \text{ M}$  and  $[\text{Fe}^{2+}] = 0.68 \text{ M}$ .

**Strategy** Because the reaction is not run under standard-state conditions (concentrations are not 1 M), we need Nernst's equation [Equation (19.8)] to calculate the emf ( $E$ ) of a hypothetical galvanic cell and determine the spontaneity of the reaction. The standard emf ( $E^\circ$ ) can be calculated using the standard reduction potentials in Table 19.1. Remember that solids do not appear in the reaction quotient ( $Q$ ) term in the Nernst equation. Note that 2 moles of electrons are transferred per mole of reaction, that is,  $n = 2$ .

**Solution** The half-cell reactions are



$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \\ &= E_{\text{Fe}^{2+}/\text{Fe}}^\circ - E_{\text{Co}^{2+}/\text{Co}}^\circ \\ &= -0.44 \text{ V} - (-0.28 \text{ V}) \\ &= -0.16 \text{ V} \end{aligned}$$

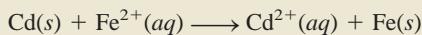
From Equation (19.8) we write

$$\begin{aligned} E &= E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q \\ &= E^\circ - \frac{0.0257 \text{ V}}{n} \ln \frac{[\text{Co}^{2+}]}{[\text{Fe}^{2+}]} \\ &= -0.16 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.15}{0.68} \\ &= -0.16 \text{ V} + 0.019 \text{ V} \\ &= -0.14 \text{ V} \end{aligned}$$

**Similar problems:** 19.29, 19.30.

Because  $E$  is negative, the reaction is not spontaneous in the direction written.

**Practice Exercise** Will the following reaction occur spontaneously at 25°C, given that  $[\text{Fe}^{2+}] = 0.60 \text{ M}$  and  $[\text{Cd}^{2+}] = 0.010 \text{ M}$ ?



Now suppose we want to determine at what ratio of  $[Co^{2+}]$  to  $[Fe^{2+}]$  the reaction in Example 19.6 would become spontaneous. We can use Equation (19.8) as follows:

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q$$

We first set  $E$  equal to zero, which corresponds to the equilibrium situation.

**When  $E = 0$ ,  $Q = K$ .**

$$\begin{aligned} 0 &= -0.16 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{[Co^{2+}]}{[Fe^{2+}]} \\ \ln \frac{[Co^{2+}]}{[Fe^{2+}]} &= -12.5 \\ \frac{[Co^{2+}]}{[Fe^{2+}]} &= e^{-12.5} = K \end{aligned}$$

or

$$K = 4 \times 10^{-6}$$

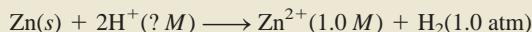
Thus, for the reaction to be spontaneous, the ratio  $[Co^{2+}]/[Fe^{2+}]$  must be smaller than  $4 \times 10^{-6}$  so that  $E$  would become positive.

As Example 19.7 shows, if gases are involved in the cell reaction, their concentrations should be expressed in atm.

### Example 19.7

Consider the galvanic cell shown in Figure 19.4(a). In a certain experiment, the emf ( $E$ ) of the cell is found to be 0.54 V at 25°C. Suppose that  $[Zn^{2+}] = 1.0 \text{ M}$  and  $P_{H_2} = 1.0 \text{ atm}$ . Calculate the molar concentration of  $H^+$ .

**Strategy** The equation that relates standard emf and nonstandard emf is the Nernst equation. The overall cell reaction is



Given the emf of the cell ( $E$ ), we apply the Nernst equation to solve for  $[H^+]$ . Note that 2 moles of electrons are transferred per mole of reaction; that is,  $n = 2$ .

**Solution** As we saw earlier (p. 649), the standard emf ( $E^\circ$ ) for the cell is 0.76 V. From Equation (19.8) we write

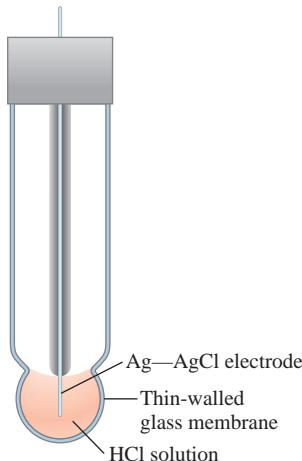
$$\begin{aligned} E &= E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q \\ &= E^\circ - \frac{0.0257 \text{ V}}{n} \ln \frac{[Zn^{2+}]P_{H_2}}{[H^+]^2} \\ 0.54 \text{ V} &= 0.76 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{(1.0)(1.0)}{[H^+]^2} \\ -0.22 \text{ V} &= \frac{0.0257 \text{ V}}{2} \ln \frac{1}{[H^+]^2} \\ 17.1 &= \ln \frac{1}{[H^+]^2} \\ e^{17.1} &= \frac{1}{[H^+]^2} \\ [H^+] &= \sqrt{\frac{1}{e^{17.1}}} = \sqrt{\frac{1}{3 \times 10^7}} = 2 \times 10^{-4} \text{ M} \end{aligned}$$

(Continued)

**Similar problem:** 19.32.

**Check** The fact that the nonstandard-state emf ( $E$ ) is given in the problem means that not all the reacting species are in their standard-state concentrations. Thus, because both  $\text{Zn}^{2+}$  ions and  $\text{H}_2$  gas are in their standard states,  $[\text{H}^+]$  is not 1  $M$ .

**Practice Exercise** What is the emf of a galvanic cell consisting of a  $\text{Cd}^{2+}/\text{Cd}$  half-cell and a  $\text{Pt}/\text{H}^+/\text{H}_2$  half-cell if  $[\text{Cd}^{2+}] = 0.20 \text{ M}$ ,  $[\text{H}^+] = 0.16 \text{ M}$ , and  $P_{\text{H}_2} = 0.80 \text{ atm}$ ?



**Figure 19.6**  
A glass electrode that is used in conjunction with a reference electrode in a pH meter.

Example 19.7 shows that a galvanic cell whose cell reaction involves  $\text{H}^+$  ions can be used to measure  $[\text{H}^+]$  or pH. The pH meter described in Section 16.3 is based on this principle. However, the hydrogen electrode (see Figure 19.3) is normally not employed in laboratory work because it is awkward to use. Instead, it is replaced by a *glass electrode*, shown in Figure 19.6. The electrode consists of a very thin glass membrane that is permeable to  $\text{H}^+$  ions. A silver wire coated with silver chloride is immersed in a dilute hydrochloric acid solution. When the electrode is placed in a solution whose pH is different from that of the inner solution, the potential difference that develops between the two sides of the membrane can be monitored using a reference electrode. The emf of the cell made up of the glass electrode and the reference electrode is measured with a voltmeter that is calibrated in pH units.

## Concentration Cells

Because electrode potential depends on ion concentrations, it is possible to construct a galvanic cell from two half-cells composed of the *same* material but differing in ion concentrations. Such a cell is called a *concentration cell*.

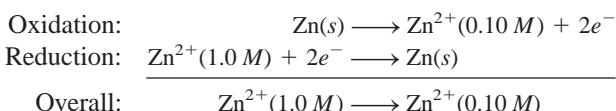
Consider a situation in which zinc electrodes are put into two aqueous solutions of zinc sulfate at 0.10  $M$  and 1.0  $M$  concentrations. The two solutions are connected by a salt bridge, and the electrodes are joined by a piece of wire in an arrangement like that shown in Figure 19.1. According to Le Châtelier's principle, the tendency for the reduction



increases with increasing concentration of  $\text{Zn}^{2+}$  ions. Therefore, reduction should occur in the more concentrated compartment and oxidation should take place on the more dilute side. The cell diagram is



and the half-reactions are



The emf of the cell is

$$E = E^\circ - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{Zn}^{2+}]_{\text{dil}}}{[\text{Zn}^{2+}]_{\text{conc}}}$$

where the subscripts "dil" and "conc" refer to the 0.10  $M$  and 1.0  $M$  concentrations, respectively. The  $E^\circ$  for this cell is zero (the same electrode and the same type of ions are involved), so

$$E = 0 - \frac{0.0257 \text{ V}}{2} \ln \frac{0.10}{1.0}$$

$$= 0.0296 \text{ V}$$

The emf of concentration cells is usually small and decreases continually during the operation of the cell as the concentrations in the two compartments approach each other. When the concentrations of the ions in the two compartments are the same,  $E$  becomes zero, and no further change occurs.

A biological cell can be compared to a concentration cell for the purpose of calculating its *membrane potential*. Membrane potential is the electrical potential that exists across the membrane of various kinds of cells, including muscle cells and nerve cells. It is responsible for the propagation of nerve impulses and heartbeat. A membrane potential is established whenever there are unequal concentrations of the same type of ion in the interior and exterior of a cell. For example, the concentrations of  $\text{K}^+$  ions in the interior and exterior of a nerve cell are 400 mM and 15 mM, respectively. Treating the situation as a concentration cell and applying the Nernst equation for just one kind of ions, we can write

$$E = E^\circ - \frac{0.0257 \text{ V}}{1} \ln \frac{[\text{K}^+]_{\text{ex}}}{[\text{K}^+]_{\text{in}}}$$

$$= -(0.0257 \text{ V}) \ln \frac{15}{400}$$

$$= 0.084 \text{ V or } 84 \text{ mV}$$

$1 \text{ mM} = 1 \times 10^{-3} \text{ M}$ .

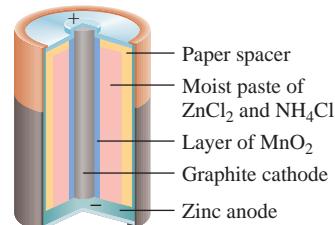
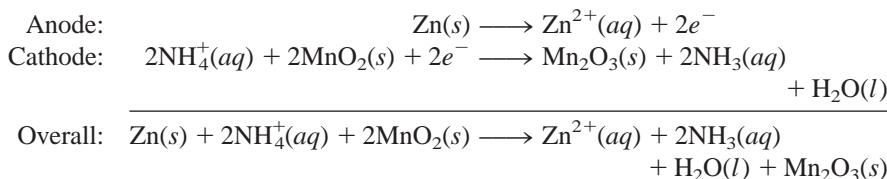
where “ex” and “in” denote exterior and interior. Note that we have set  $E^\circ = 0$  because the same type of ion is involved. Thus, an electrical potential of 84 mV exists across the membrane due to the unequal concentrations of  $\text{K}^+$  ions.

## 19.6 Batteries

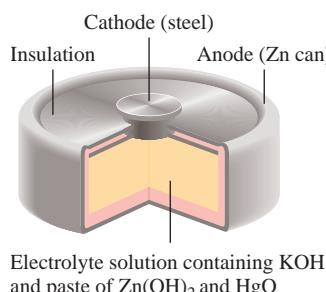
A **battery** is a galvanic cell, or a series of combined galvanic cells, that can be used as a source of direct electric current at a constant voltage. Although the operation of a battery is similar in principle to that of the galvanic cells described in Section 19.2, a battery has the advantage of being completely self-contained and requiring no auxiliary components such as salt bridges. Here we will discuss several types of batteries that are in widespread use.

### The Dry Cell Battery

The most common dry cell, that is, a cell without a fluid component, is the *Leclanché cell* used in flashlights and transistor radios. The anode of the cell consists of a zinc can or container that is in contact with manganese dioxide ( $\text{MnO}_2$ ) and an electrolyte. The electrolyte consists of ammonium chloride and zinc chloride in water, to which starch is added to thicken the solution to a pastelike consistency so that it is less likely to leak (Figure 19.7). A carbon rod serves as the cathode, which is immersed in the electrolyte in the center of the cell. The cell reactions are



**Figure 19.7**  
Interior section of a dry cell of the kind used in flashlights and transistor radios. Actually, the cell is not completely dry, as it contains a moist electrolyte paste.

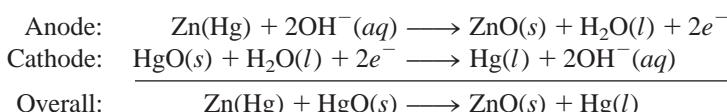


**Figure 19.8**  
*Interior section of a mercury battery.*

Actually, this equation is an oversimplification of a complex process. The voltage produced by a dry cell is about 1.5 V.

### The Mercury Battery

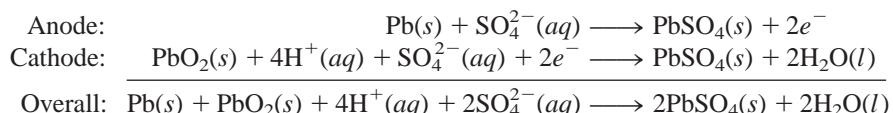
The mercury battery is used extensively in medicine and electronic industries and is more expensive than the common dry cell. Contained in a stainless steel cylinder, the mercury battery consists of a zinc anode (amalgamated with mercury) in contact with a strongly alkaline electrolyte containing zinc oxide and mercury(II) oxide (Figure 19.8). The cell reactions are



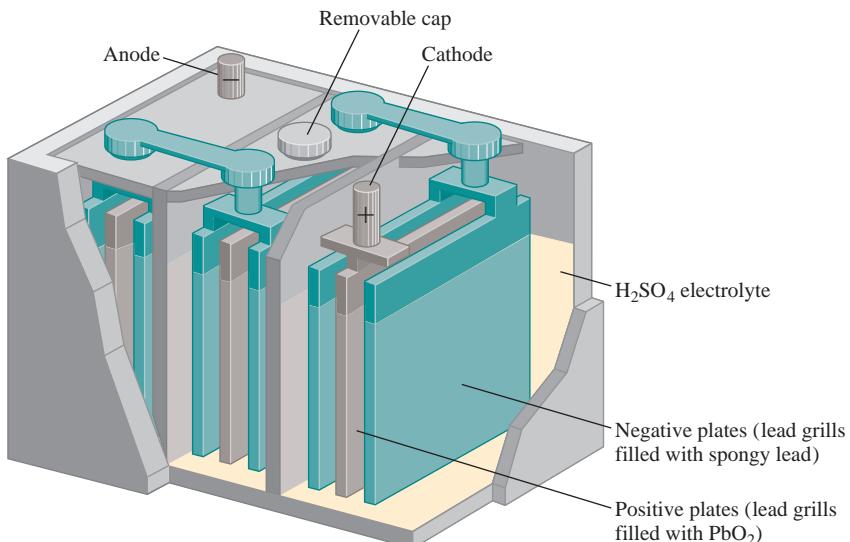
Because there is no change in electrolyte composition during operation—the overall cell reaction involves only solid substances—the mercury battery provides a more constant voltage (1.35 V) than the Leclanché cell. It also has a considerably higher capacity and longer life. These qualities make the mercury battery ideal for use in pacemakers, hearing aids, electric watches, and light meters.

### The Lead Storage Battery

The lead storage battery commonly used in automobiles consists of six identical cells joined together in series. Each cell has a lead anode and a cathode made of lead dioxide ( $\text{PbO}_2$ ) packed on a metal plate (Figure 19.9). Both the cathode and the anode are immersed in an aqueous solution of sulfuric acid, which acts as the electrolyte. The cell reactions are

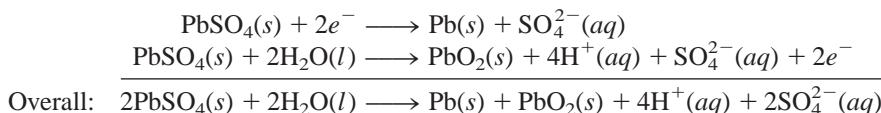


**Figure 19.9**  
*Interior section of a lead storage battery. Under normal operating conditions, the concentration of the sulfuric acid solution is about 38 percent by mass.*



Under normal operating conditions, each cell produces 2 V; a total of 12 V from the six cells is used to power the ignition circuit of the automobile and its other electrical systems. The lead storage battery can deliver large amounts of current for a short time, such as the time it takes to start up the engine.

Unlike the Leclanché cell and the mercury battery, the lead storage battery is rechargeable. Recharging the battery means reversing the normal electrochemical reaction by applying an external voltage at the cathode and the anode. (This kind of process is called *electrolysis*, see p. 668.) The reactions that replenish the original materials are



The overall reaction is exactly the opposite of the normal cell reaction.

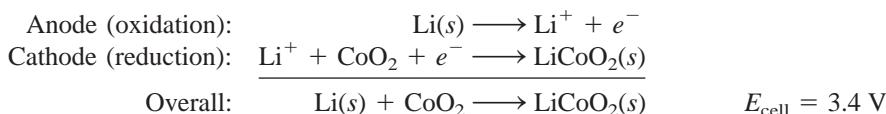
Two aspects of the operation of a lead storage battery are worth noting. First, because the electrochemical reaction consumes sulfuric acid, the degree to which the battery has been discharged can be checked by measuring the density of the electrolyte with a *hydrometer*, as is usually done at gas stations. The density of the fluid in a “healthy,” fully charged battery should be equal to or greater than 1.2 g/mL. Second, people living in cold climates sometimes have trouble starting their cars because the battery has “gone dead.” Thermodynamic calculations show that the emf of many galvanic cells decreases with decreasing temperature. However, for a lead storage battery, the temperature coefficient is about  $1.5 \times 10^{-4}$  V/°C; that is, there is a decrease in voltage of  $1.5 \times 10^{-4}$  V for every degree drop in temperature. Thus, even allowing for a 40°C change in temperature, the decrease in voltage amounts to only  $6 \times 10^{-3}$  V, which is about

$$\frac{6 \times 10^{-3} \text{ V}}{12 \text{ V}} \times 100\% = 0.05\%$$

of the operating voltage, an insignificant change. The real cause of a battery’s apparent breakdown is an increase in the viscosity of the electrolyte as the temperature decreases. For the battery to function properly, the electrolyte must be fully conducting. However, the ions move much more slowly in a viscous medium, so the resistance of the fluid increases, leading to a decrease in the power output of the battery. If an apparently “dead battery” is warmed to near room temperature on a frigid day, it recovers its ability to deliver normal power.

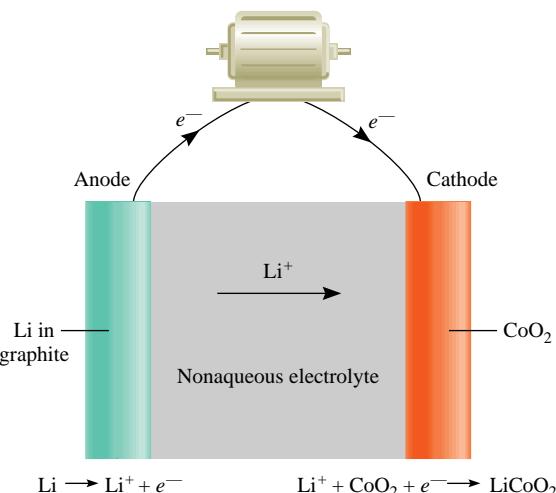
## The Lithium-Ion Battery

Figure 19.10 shows a schematic diagram of a lithium-ion battery. The anode is made of a conducting carbonaceous material, usually graphite, which has tiny spaces in its structure that can hold both Li atoms and Li<sup>+</sup> ions. The cathode is made of a transition metal oxide such as CoO<sub>2</sub>, which can also hold Li<sup>+</sup> ions. Because of the high reactivity of the metal, nonaqueous electrolyte (organic solvent plus dissolved salt) must be used. During the discharge of the battery, the half-cell reactions are



**Figure 19.10**

A lithium-ion battery. Lithium atoms are embedded in the graphite, which serves as the anode and  $\text{CoO}_2$  is the cathode. During operation,  $\text{Li}^+$  ions migrate through the nonaqueous electrolyte from the anode to the cathode while electrons flow externally from the anode to the cathode to complete the circuit.



The advantage of the battery is that lithium has the most negative standard reduction potential (see Table 19.1) and hence the greatest reducing strength. Furthermore, lithium is the lightest metal so that only 6.941 g of Li (its molar mass) are needed to produce 1 mole of electrons. A lithium-ion battery can be recharged literally hundreds of times without deterioration. These desirable characteristics make it suitable for use in cellular telephones, digital cameras, and laptop computers.

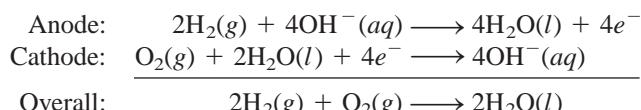
## Fuel Cells

Fossil fuels are a major source of energy, but conversion of fossil fuel into electrical energy is a highly inefficient process. Consider the combustion of methane:



To generate electricity, heat produced by the reaction is first used to convert water to steam, which then drives a turbine that drives a generator. An appreciable fraction of the energy released in the form of heat is lost to the surroundings at each step; even the most efficient power plant converts only about 40 percent of the original chemical energy into electricity. Because combustion reactions are redox reactions, it is more desirable to carry them out directly by electrochemical means, thereby greatly increasing the efficiency of power production. This objective can be accomplished by a device known as a ***fuel cell***, a galvanic cell that requires a continuous supply of reactants to keep functioning.

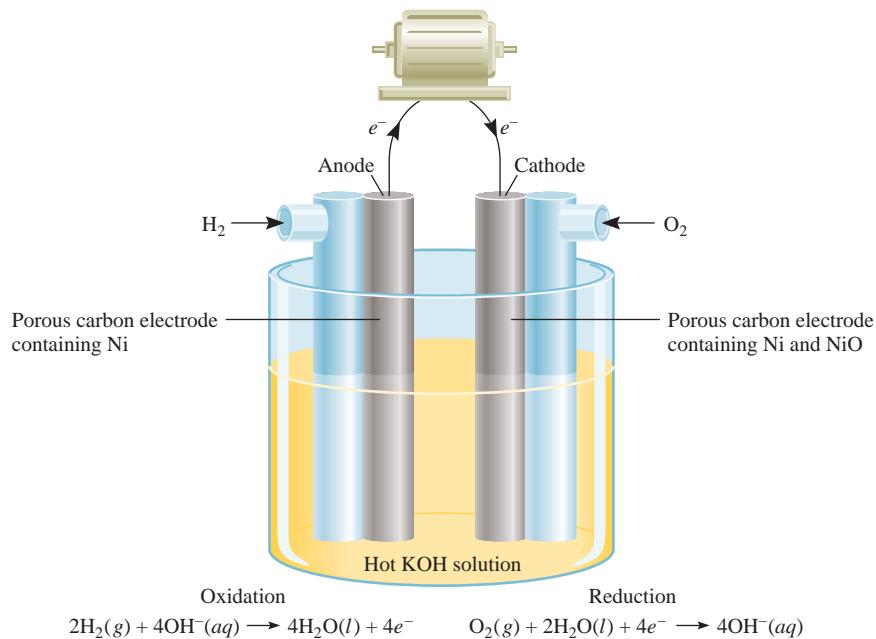
In its simplest form, a hydrogen-oxygen fuel cell consists of an electrolyte solution, such as potassium hydroxide solution, and two inert electrodes. Hydrogen and oxygen gases are bubbled through the anode and cathode compartments (Figure 19.11), where the following reactions take place:



The standard emf of the cell can be calculated as follows, with data from Table 19.1:

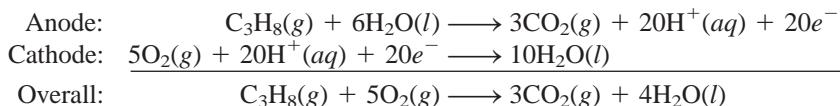
$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \\ &= 0.40 \text{ V} - (-0.83 \text{ V}) \\ &= 1.23 \text{ V} \end{aligned}$$

The positive standard emf means that the process will occur spontaneously.



Thus, the cell reaction is spontaneous under standard-state conditions. Note that the reaction is the same as the hydrogen combustion reaction, but the oxidation and reduction are carried out separately at the anode and the cathode. Like platinum in the standard hydrogen electrode, the electrodes have a twofold function. They serve as electrical conductors, and they provide the necessary surfaces for the initial decomposition of the molecules into atomic species, prior to electron transfer. They are *electrocatalysts*. Metals such as platinum, nickel, and rhodium are good electrocatalysts.

In addition to the H<sub>2</sub>-O<sub>2</sub> system, a number of other fuel cells have been developed. Among these is the propane-oxygen fuel cell. The half-cell reactions are



The overall reaction is identical to the burning of propane in oxygen.

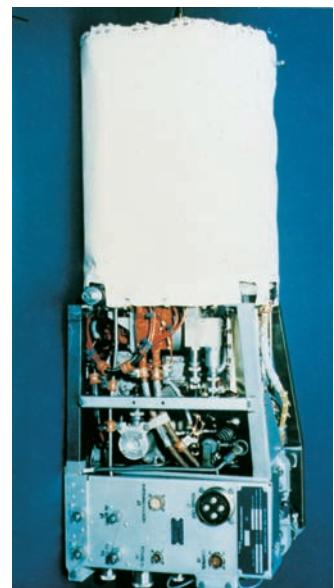
Unlike batteries, fuel cells do not store chemical energy. Reactants must be constantly resupplied, and products must be constantly removed from a fuel cell. In this respect, a fuel cell resembles an engine more than it does a battery.

Properly designed fuel cells may be as much as 70 percent efficient, about twice as efficient as an internal combustion engine. In addition, fuel-cell generators are free of the noise, vibration, heat transfer, thermal pollution, and other problems normally associated with conventional power plants. Nevertheless, fuel cells are not yet in widespread use. A major problem lies in the lack of cheap electrocatalysts able to function efficiently for long periods of time without contamination. The most successful application of fuel cells to date has been in space vehicles (Figure 19.12).

**Figure 19.11**  
A hydrogen-oxygen fuel cell. The Ni and NiO embedded in the porous carbon electrodes are electrocatalysts.



A car powered by hydrogen fuel cells manufactured by General Motors.



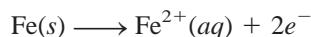
**Figure 19.12**  
A hydrogen-oxygen fuel cell used in the space program. The pure water produced by the cell is consumed by the astronauts.

## 19.7 Corrosion

**Corrosion** is the term usually applied to *the deterioration of metals by an electrochemical process*. We see many examples of corrosion around us. Rust on iron, tarnish on silver, and the green patina formed on copper and brass are a few of them. Corrosion

causes enormous damage to buildings, bridges, ships, and cars. The cost of metallic corrosion to the U.S. economy has been estimated to be well over 100 billion dollars a year! This section discusses some of the fundamental processes that occur in corrosion and methods used to protect metals against it.

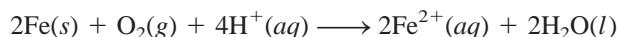
By far the most familiar example of corrosion is the formation of rust on iron. Oxygen gas and water must be present for iron to rust. Although the reactions involved are quite complex and not completely understood, the main steps are believed to be as follows. A region of the metal's surface serves as the anode, where oxidation occurs:



The electrons given up by iron reduce atmospheric oxygen to water at the cathode, which is another region of the same metal's surface:



The overall redox reaction is

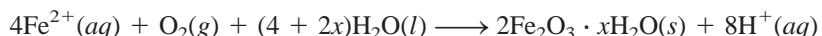


With data from Table 19.1, we find the standard emf for this process:

$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \\ &= 1.23 \text{ V} - (-0.44 \text{ V}) \\ &= 1.67 \text{ V} \end{aligned}$$

Note that this reaction occurs in an acidic medium; the  $\text{H}^+$  ions are supplied in part by the reaction of atmospheric carbon dioxide with water to form  $\text{H}_2\text{CO}_3$ .

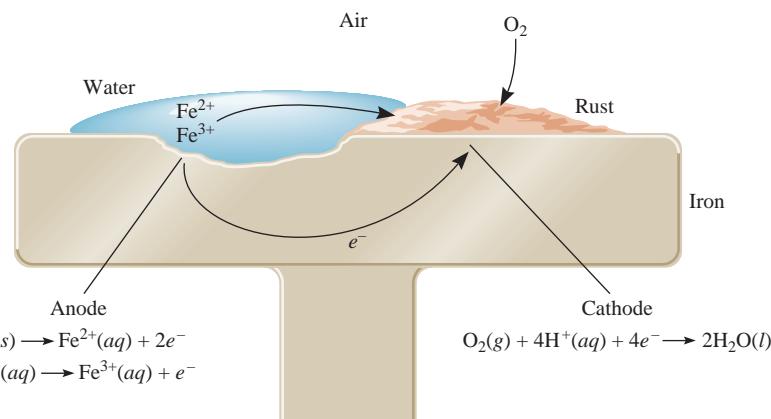
The  $\text{Fe}^{2+}$  ions formed at the anode are further oxidized by oxygen:



This hydrated form of iron(III) oxide is known as rust. The amount of water associated with the iron oxide varies, so we represent the formula as  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ .

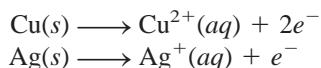
Figure 19.13 shows the mechanism of rust formation. The electrical circuit is completed by the migration of electrons and ions; this is why rusting occurs so rapidly in salt water. In cold climates, salts ( $\text{NaCl}$  or  $\text{CaCl}_2$ ) spread on roadways to melt ice and snow are a major cause of rust formation on automobiles.

**Figure 19.13**  
The electrochemical process involved in rust formation.  
The  $\text{H}^+$  ions are supplied by  $\text{H}_2\text{CO}_3$ , which forms when  $\text{CO}_2$  dissolves in water.



Metallic corrosion is not limited to iron. Consider aluminum, a metal used to make many useful things, including airplanes and beverage cans. Aluminum has a much greater tendency to oxidize than iron does; in Table 19.1 we see that Al has a more negative standard reduction potential than Fe. Based on this fact alone, we might expect to see airplanes slowly corrode away in rainstorms, and soda cans transformed into piles of corroded aluminum. These processes do not occur because the layer of insoluble aluminum oxide ( $\text{Al}_2\text{O}_3$ ) that forms on its surface when the metal is exposed to air serves to protect the aluminum underneath from further corrosion. The rust that forms on the surface of iron, however, is too porous to protect the underlying metal.

Coinage metals such as copper and silver also corrode, but much more slowly.

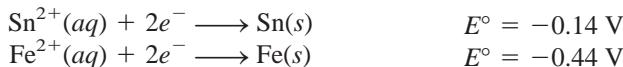


In normal atmospheric exposure, copper forms a layer of copper carbonate ( $\text{CuCO}_3$ ), a green substance also called patina, that protects the metal underneath from further corrosion. Likewise, silverware that comes into contact with foodstuffs develops a layer of silver sulfide ( $\text{Ag}_2\text{S}$ ).

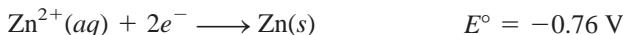
A number of methods have been devised to protect metals from corrosion. Most of these methods are aimed at preventing rust formation. The most obvious approach is to coat the metal surface with paint. However, if the paint is scratched, pitted, or dented to expose even the smallest area of bare metal, rust will form under the paint layer. The surface of iron metal can be made inactive by a process called *passivation*. A thin oxide layer is formed when the metal is treated with a strong oxidizing agent such as concentrated nitric acid. A solution of sodium chromate is often added to cooling systems and radiators to prevent rust formation.

The tendency for iron to oxidize is greatly reduced when it is alloyed with certain other metals. For example, in stainless steel, an alloy of iron and chromium, a layer of chromium oxide forms that protects the iron from corrosion.

An iron container can be covered with a layer of another metal such as tin or zinc. A “tin” can is made by applying a thin layer of tin over iron. Rust formation is prevented as long as the tin layer remains intact. However, once the surface has been scratched, rusting occurs rapidly. If we look up the standard reduction potentials, according to the diagonal rule, we find that iron acts as the anode and tin as the cathode in the corrosion process:



The protective process is different for zinc-plated, or *galvanized*, iron. Zinc is more easily oxidized than iron (see Table 19.1):



So even if a scratch exposes the iron, the zinc is still attacked. In this case, the zinc metal serves as the anode and the iron is the cathode.

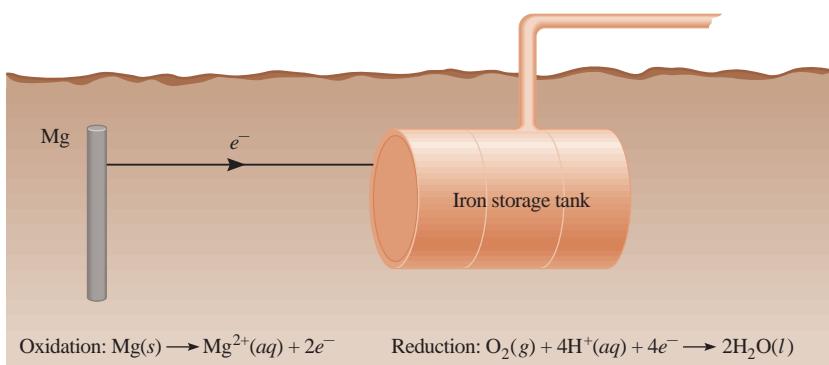
*Cathodic protection* is a process in which the metal that is to be protected from corrosion is made the cathode in what amounts to a galvanic cell. Figure 19.14 shows how an iron nail can be protected from rusting by connecting the nail to a piece of zinc. Without such protection, an iron nail quickly rusts in water. Rusting of underground iron pipes and iron storage tanks can be prevented or greatly reduced by connecting them to metals such as zinc and magnesium, which oxidize more readily than iron (Figure 19.15).



**Figure 19.14**  
An iron nail that is cathodically protected by a piece of zinc strip does not rust in water, while an iron nail without such protection rusts readily.

**Figure 19.15**

*Cathodic protection of an iron storage tank (cathode) by magnesium, a more electropositive metal (anode). Because only the magnesium is depleted in the electrochemical process, it is sometimes called the sacrificial anode.*



## 19.8 Electrolysis

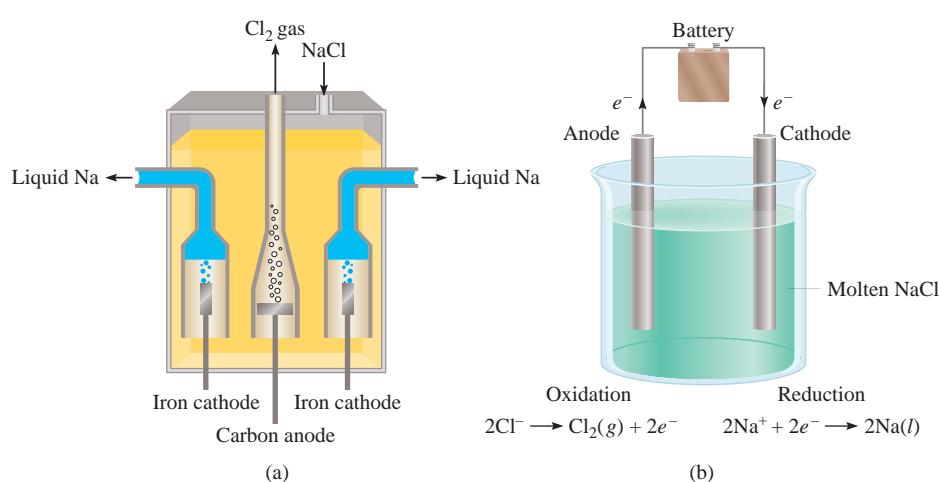
In contrast to spontaneous redox reactions, which result in the conversion of chemical energy into electrical energy, **electrolysis** is the process in which *electrical energy is used to cause a nonspontaneous chemical reaction to occur*. An **electrolytic cell** is an apparatus for carrying out electrolysis. The same principles underlie electrolysis and the processes that take place in galvanic cells. Here we will discuss three examples of electrolysis based on those principles. Then we will look at the quantitative aspects of electrolysis.

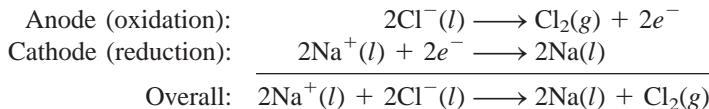
### Electrolysis of Molten Sodium Chloride

In its molten state, sodium chloride, an ionic compound, can be electrolyzed to form sodium metal and chlorine. Figure 19.16(a) is a diagram of a *Downs cell*, which is used for large-scale electrolysis of NaCl. In molten NaCl, the cations and anions are the  $\text{Na}^+$  and  $\text{Cl}^-$  ions, respectively. Figure 19.16(b) is a simplified diagram showing the reactions that occur at the electrodes. The electrolytic cell contains a pair of electrodes connected to the battery. The battery serves as an “electron pump,” driving electrons to the cathode, where reduction occurs, and withdrawing electrons from the anode, where oxidation occurs. The reactions at the electrodes are

**Figure 19.16**

(a) A practical arrangement called a *Downs cell* for the electrolysis of molten NaCl (*m.p.* = 801°C). The sodium metal formed at the cathodes is in the liquid state. Because liquid sodium metal is less dense than molten NaCl, the sodium floats to the surface, as shown, and is collected. Chlorine gas forms at the anode and is collected at the top. (b) A simplified diagram showing the electrode reactions during the electrolysis of molten NaCl. The battery is needed to drive the nonspontaneous reactions.



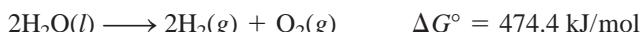


This process is a major source of pure sodium metal and chlorine gas.

Theoretical estimates show that the  $E^\circ$  value for the overall process is about  $-4$  V, which means that this is a nonspontaneous process. Therefore, a *minimum* of  $4$  V must be supplied by the battery to carry out the reaction. In practice, a higher voltage is necessary because of inefficiencies in the electrolytic process and because of overvoltage, to be discussed shortly.

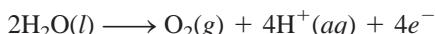
## Electrolysis of Water

Water in a beaker under atmospheric conditions ( $1$  atm and  $25^\circ\text{C}$ ) will not spontaneously decompose to form hydrogen and oxygen gas because the standard free-energy change for the reaction is a large positive quantity:

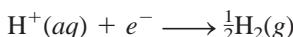


However, this reaction can be induced in a cell like the one shown in Figure 19.17. This electrolytic cell consists of a pair of electrodes made of a nonreactive metal, such as platinum, immersed in water. When the electrodes are connected to the battery, nothing happens because there are not enough ions in pure water to carry much of an electric current. (Remember that at  $25^\circ\text{C}$ , pure water has only  $1 \times 10^{-7} M$   $\text{H}^+$  ions and  $1 \times 10^{-7} M$   $\text{OH}^-$  ions.) On the other hand, the reaction occurs readily in a  $0.1 M$   $\text{H}_2\text{SO}_4$  solution because there are a sufficient number of ions to conduct electricity. Immediately, gas bubbles begin to appear at both electrodes.

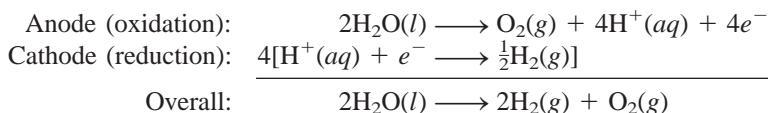
Figure 19.18 shows the electrode reactions. The process at the anode is



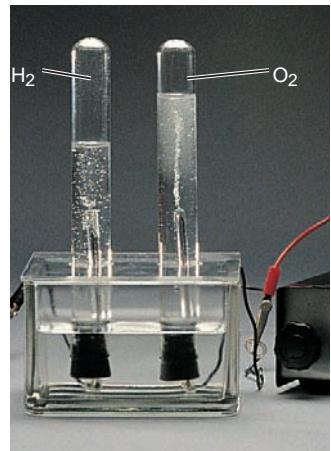
while at the cathode we have



The overall reaction is given by

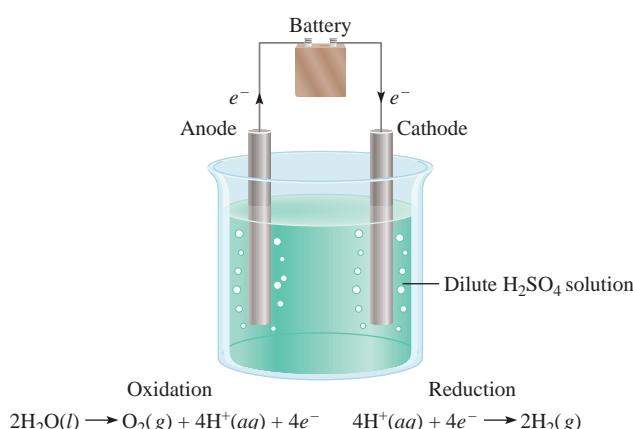


Note that no net  $\text{H}_2\text{SO}_4$  is consumed.



**Figure 19.17**  
Apparatus for small-scale electrolysis of water. The volume of hydrogen gas generated (left column) is twice that of oxygen gas (right column).

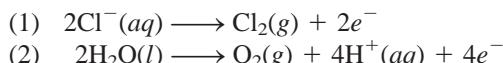
What is the minimum voltage needed for this electrolytic process?



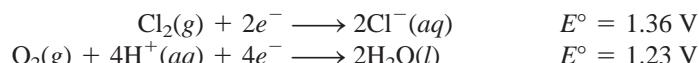
**Figure 19.18**  
A diagram showing the electrode reactions during the electrolysis of water.

## Electrolysis of an Aqueous Sodium Chloride Solution

This is the most complicated of the three examples of electrolysis considered here because aqueous sodium chloride solution contains several species that could be oxidized and reduced. The oxidation reactions that might occur at the anode are



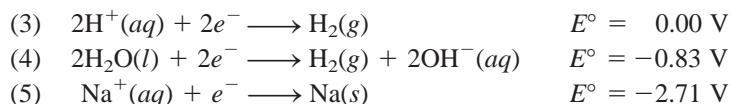
Referring to Table 19.1, we find



**Because  $\text{Cl}_2$  is more easily reduced than  $\text{O}_2$ , it follows that it would be more difficult to oxidize  $\text{Cl}^-$  than  $\text{H}_2\text{O}$  at the anode.**

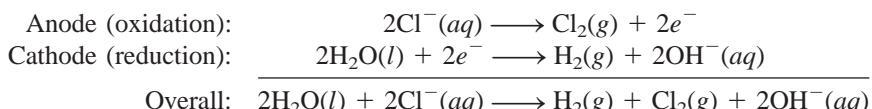
The standard reduction potentials of (1) and (2) are not very different, but the values do suggest that  $\text{H}_2\text{O}$  should be preferentially oxidized at the anode. However, by experiment we find that the gas liberated at the anode is  $\text{Cl}_2$ , not  $\text{O}_2$ ! In studying electrolytic processes, we sometimes find that the voltage required for a reaction is considerably higher than the electrode potential indicates. The **overvoltage** is the difference between the electrode potential and the actual voltage required to cause electrolysis. The overvoltage for  $\text{O}_2$  formation is quite high. Therefore, under normal operating conditions  $\text{Cl}_2$  gas is actually formed at the anode instead of  $\text{O}_2$ .

The reductions that might occur at the cathode are



Reaction (5) is ruled out because it has a very negative standard reduction potential. Reaction (3) is preferred over (4) under standard-state conditions. At a pH of 7 (as is the case for a  $\text{NaCl}$  solution), however, they are equally probable. We generally use (4) to describe the cathode reaction because the concentration of  $\text{H}^+$  ions is too low (about  $1 \times 10^{-7} \text{ M}$ ) to make (3) a reasonable choice.

Thus, the half-cell reactions in the electrolysis of aqueous sodium chloride are



As the overall reaction shows, the concentration of the  $\text{Cl}^-$  ions decreases during electrolysis and that of the  $\text{OH}^-$  ions increases. Therefore, in addition to  $\text{H}_2$  and  $\text{Cl}_2$ , the useful by-product  $\text{NaOH}$  can be obtained by evaporating the aqueous solution at the end of the electrolysis.

Keep in mind the following from our analysis of electrolysis: cations are likely to be reduced at the cathode and anions are likely to be oxidized at the anode, and in aqueous solutions water itself may be oxidized and/or reduced. The outcome depends on the nature of other species present.

### Example 19.8

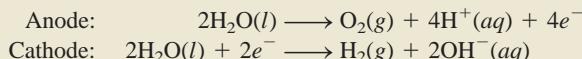
An aqueous  $\text{Na}_2\text{SO}_4$  solution is electrolyzed, using the apparatus shown in Figure 19.17. If the products formed at the anode and cathode are oxygen gas and hydrogen gas, respectively, describe the electrolysis in terms of the reactions at the electrodes.

(Continued)

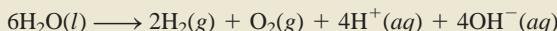
**Strategy** Before we look at the electrode reactions, we should consider the following facts: (1) Because  $\text{Na}_2\text{SO}_4$  does not hydrolyze, the pH of the solution is close to 7. (2) The  $\text{Na}^+$  ions are not reduced at the cathode and the  $\text{SO}_4^{2-}$  ions are not oxidized at the anode. These conclusions are drawn from the electrolysis of water in the presence of sulfuric acid and in aqueous sodium chloride solution, as discussed earlier. Therefore, both the oxidation and reduction reactions involve only water molecules.

The  $\text{SO}_4^{2-}$  ion is the conjugate base of the weak acid  $\text{HSO}_4^-$  ( $K_a = 1.3 \times 10^{-2}$ ). However, the extent to which  $\text{SO}_4^{2-}$  hydrolyzes is negligible. Also, the  $\text{SO}_4^{2-}$  ion is not oxidized at the anode.

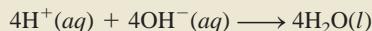
**Solution** The electrode reactions are



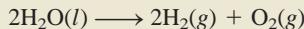
The overall reaction, obtained by doubling the cathode reaction coefficients and adding the result to the anode reaction, is



If the  $\text{H}^+$  and  $\text{OH}^-$  ions are allowed to mix, then



and the overall reaction becomes



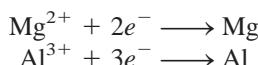
**Similar problem:** 19.46(a).

**Practice Exercise** An aqueous solution of  $\text{Mg}(\text{NO}_3)_2$  is electrolyzed. What are the gaseous products at the anode and cathode?

Electrolysis has many important applications in industry, mainly in the extraction and purification of metals. We will discuss some of these applications in Section 19.9.

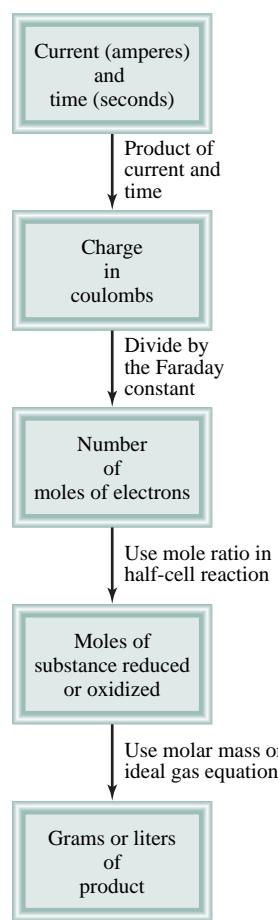
## Quantitative Aspects of Electrolysis

The quantitative treatment of electrolysis was developed primarily by Faraday. He observed that the mass of product formed (or reactant consumed) at an electrode is proportional to both the amount of electricity transferred at the electrode and the molar mass of the substance in question. For example, in the electrolysis of molten  $\text{NaCl}$ , the cathode reaction tells us that one  $\text{Na}$  atom is produced when one  $\text{Na}^+$  ion accepts an electron from the electrode. To reduce 1 mole of  $\text{Na}^+$  ions, we must supply Avogadro's number ( $6.02 \times 10^{23}$ ) of electrons to the cathode. On the other hand, the stoichiometry of the anode reaction shows that oxidation of two  $\text{Cl}^-$  ions yields one chlorine molecule. Therefore, the formation of 1 mole of  $\text{Cl}_2$  results in the transfer of 2 moles of electrons from the  $\text{Cl}^-$  ions to the anode. Similarly, it takes 2 moles of electrons to reduce 1 mole of  $\text{Mg}^{2+}$  ions and 3 moles of electrons to reduce 1 mole of  $\text{Al}^{3+}$  ions:



In an electrolysis experiment, we generally measure the current (in amperes, A) that passes through an electrolytic cell in a given period of time. The relationship between charge (in coulombs, C) and current is

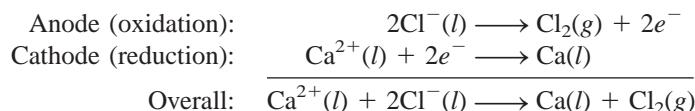
$$1 \text{ C} = 1 \text{ A} \times 1 \text{ s}$$



**Figure 19.19**  
Steps involved in calculating amounts of substances reduced or oxidized in electrolysis.

that is, a coulomb is the quantity of electrical charge passing any point in the circuit in 1 second when the current is 1 ampere.

Figure 19.19 shows the steps involved in calculating the quantities of substances produced in electrolysis. Let us illustrate the approach by considering molten  $\text{CaCl}_2$  in an electrolytic cell. Suppose a current of 0.452 A is passed through the cell for 1.50 h. How much product will be formed at the anode and at the cathode? In solving electrolysis problems of this type, the first step is to determine which species will be oxidized at the anode and which species will be reduced at the cathode. Here the choice is straightforward because we only have  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  ions in molten  $\text{CaCl}_2$ . Thus, we write the half- and overall cell reactions as



The quantities of calcium metal and chlorine gas formed depend on the number of electrons that pass through the electrolytic cell, which in turn depends on current  $\times$  time, or charge:

$$? \text{ C} = 0.452 \cancel{\text{A}} \times 1.50 \cancel{\text{h}} \times \frac{3600 \cancel{\text{s}}}{1 \cancel{\text{h}}} \times \frac{1 \text{ C}}{1 \cancel{\text{A}} \cdot \cancel{\text{s}}} = 2.44 \times 10^3 \text{ C}$$

Because 1 mol  $e^-$  = 96,500 C and 2 mol  $e^-$  are required to reduce 1 mole of  $\text{Ca}^{2+}$  ions, the mass of Ca metal formed at the cathode is calculated as follows:

$$? \text{ g Ca} = 2.44 \times 10^3 \cancel{\text{C}} \times \frac{1 \cancel{\text{mol } e^-}}{96,500 \cancel{\text{C}}} \times \frac{1 \cancel{\text{mol Ca}}}{2 \cancel{\text{mol } e^-}} \times \frac{40.08 \text{ g Ca}}{1 \cancel{\text{mol Ca}}} = 0.507 \text{ g Ca}$$

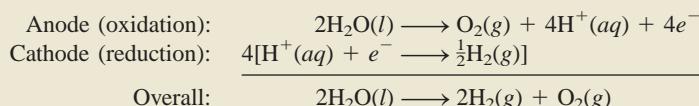
The anode reaction indicates that 1 mole of chlorine is produced per 2 mol  $e^-$  of electricity. Hence the mass of chlorine gas formed is

$$? \text{ g Cl}_2 = 2.44 \times 10^3 \cancel{\text{C}} \times \frac{1 \cancel{\text{mol } e^-}}{96,500 \cancel{\text{C}}} \times \frac{1 \cancel{\text{mol Cl}_2}}{2 \cancel{\text{mol } e^-}} \times \frac{70.90 \text{ g Cl}_2}{1 \cancel{\text{mol Cl}_2}} = 0.896 \text{ g Cl}_2$$

### Example 19.9

A current of 1.26 A is passed through an electrolytic cell containing a dilute sulfuric acid solution for 7.44 h. Write the half-cell reactions and calculate the volume of gases generated at STP.

**Strategy** Earlier (see p. 669) we saw that the half-cell reactions for the process are



According to Figure 19.19, we carry out the following conversion steps to calculate the quantity of  $\text{O}_2$  in moles:

$$\text{current} \times \text{time} \rightarrow \text{coulombs} \rightarrow \text{moles of } e^- \rightarrow \text{moles of O}_2$$

Then, using the ideal gas equation we can calculate the volume of  $\text{O}_2$  in liters at STP. A similar procedure can be used for  $\text{H}_2$ .

(Continued)

**Solution** First we calculate the number of coulombs of electricity that pass through the cell:

$$\text{? C} = 1.26 \text{ A} \times 7.44 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} = 3.77 \times 10^4 \text{ C}$$

Next, we convert number of coulombs to number of moles of electrons

$$3.37 \times 10^4 \text{ C} \times \frac{1 \text{ mol } e^-}{96,500 \text{ C}} = 0.349 \text{ mol } e^-$$

From the oxidation half-reaction we see that  $1 \text{ mol O}_2 \approx 4 \text{ mol } e^-$ . Therefore, the number of moles of  $\text{O}_2$  generated is

$$0.349 \cancel{\text{mol } e^-} \times \frac{1 \text{ mol O}_2}{4 \cancel{\text{mol } e^-}} = 0.0873 \text{ mol O}_2$$

The volume of 0.0873 mol  $\text{O}_2$  at STP is given by

$$V = \frac{nRT}{P} \\ = \frac{(0.0873 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(273 \text{ K})}{1 \text{ atm}} = 1.96 \text{ L}$$

The procedure for hydrogen is similar. To simplify, we combine the first two steps to calculate the number of moles of  $\text{H}_2$  generated:

$$3.37 \times 10^4 \text{ C} \times \frac{1 \cancel{\text{mol } e^-}}{96,500 \text{ C}} \times \frac{1 \text{ mol H}_2}{2 \cancel{\text{mol } e^-}} = 0.175 \text{ mol H}_2$$

The volume of 0.175 mol  $\text{H}_2$  at STP is given by

$$V = \frac{nRT}{P} \\ = \frac{(0.175 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(273 \text{ K})}{1 \text{ atm}} \\ = 3.92 \text{ L}$$

**Check** Note that the volume of  $\text{H}_2$  is twice that of  $\text{O}_2$  (see Figure 19.17), which is what we would expect based on Avogadro's law (at the same temperature and pressure, volume is directly proportional to the number of moles of gases).

**Similar problem: 19.49.**

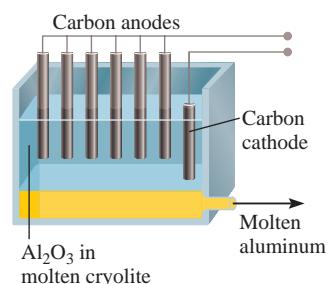
**Practice Exercise** A constant current is passed through an electrolytic cell containing molten  $\text{MgCl}_2$  for 18 h. If  $4.8 \times 10^5 \text{ g}$  of  $\text{Cl}_2$  are obtained, what is the current in amperes?

## 19.9 Electrometallurgy

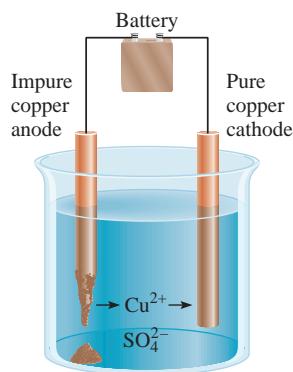
Electrolysis methods are useful for obtaining a pure metal from its ores or for refining (purifying) the metal. Collectively, these processes are called *electrometallurgy*. In the last section we saw how an active metal, sodium, can be obtained by electrolytically reducing its cation in the molten  $\text{NaCl}$  salt (p. 668). Here we will consider two other examples.

### Production of Aluminum Metal

Aluminum is usually prepared from bauxite ore ( $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ). The ore is first treated to remove various impurities and then heated to obtain the anhydrous  $\text{Al}_2\text{O}_3$ . The oxide is dissolved in molten cryolite ( $\text{Na}_3\text{AlF}_6$ ) in a Hall electrolytic cell (Figure 19.20). The

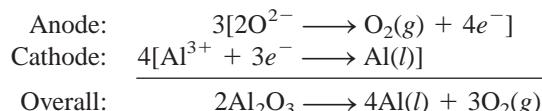


**Figure 19.20**  
Electrolytic production of aluminum based on the Hall process.



**Figure 19.21**  
Electrolytic purification of copper.

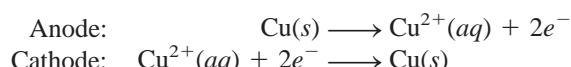
cell contains a series of carbon anodes; the cathode is also made of carbon and constitutes the lining inside the cell. The solution is electrolyzed to produce aluminum and oxygen gas:



Oxygen gas reacts with the carbon anodes at 1000°C (the melting point of cryolite) to form carbon monoxide, which escapes as a gas. The liquid aluminum metal (m.p. 660°C) sinks to the bottom of the vessel, from which it can be drained.

### Purification of Copper Metal

The copper metal obtained from its ores usually contains a number of impurities such as zinc, iron, silver, and gold. The more electropositive metals are removed by an electrolysis process in which the impure copper acts as the anode and *pure* copper acts as the cathode in a sulfuric acid solution containing Cu<sup>2+</sup> ions (Figure 19.21). The half-reactions are



Reactive metals in the copper anode, such as iron and zinc, are also oxidized at the anode and enter the solution as Fe<sup>2+</sup> and Zn<sup>2+</sup> ions. They are not reduced at the cathode, however. The less electropositive metals, such as gold and silver, are not oxidized at the anode. Eventually, as the copper anode oxidizes, these metals fall to the bottom of the cell. Thus, the net result of this electrolysis process is the transfer of copper from the anode to the cathode. Copper prepared this way has a purity greater than 99.5 percent. It is interesting to note that the metal impurities (mostly silver and gold) from the copper anode are valuable by-products, the sale of which often pays for the electricity used to drive the electrolysis.

### KEY EQUATIONS

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \quad (19.1)$$

$$\Delta G = -nFE_{\text{cell}}^{\circ} \quad (19.2)$$

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} \quad (19.3)$$

$$E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln K \quad (19.4)$$

$$E_{\text{cell}}^{\circ} = \frac{0.0257 \text{ V}}{n} \ln K \quad (19.5)$$

$$E_{\text{cell}}^{\circ} = \frac{0.0592 \text{ V}}{n} \log K \quad (19.6)$$

$$E = E^{\circ} - \frac{RT}{nF} \ln Q \quad (19.7)$$

$$E = E^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q \quad (19.8)$$

$$E = E^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q \quad (19.9)$$

Calculating the standard emf of a galvanic cell.

Relating free-energy change to the emf of the cell.

Relating the standard free-energy change to the standard emf of the cell.

Relating the standard emf of the cell to the equilibrium constant.

Relating the standard emf of the cell to the equilibrium constant at 298 K.

Relating the standard emf of the cell to the equilibrium constant at 298 K.

The Nernst equation. For calculating the emf of a cell under non-standard-state conditions.

The Nernst equation. For calculating the emf of a cell under non-standard-state conditions at 298 K.

The Nernst equation. For calculating the emf of a cell under non-standard-state conditions at 298 K.

## SUMMARY OF FACTS AND CONCEPTS

- Redox reactions involve the transfer of electrons. Equations representing redox processes can be balanced using the half-reaction method.
- All electrochemical reactions involve the transfer of electrons and therefore are redox reactions.
- In a galvanic cell, electricity is produced by a spontaneous chemical reaction. Oxidation and reduction take place separately at the anode and cathode, respectively, and the electrons flow through an external circuit.
- The two parts of a galvanic cell are the half-cells, and the reactions at the electrodes are the half-cell reactions. A salt bridge allows ions to flow between the half-cells.
- The electromotive force (emf) of a cell is the voltage difference between the two electrodes. In the external circuit, electrons flow from the anode to the cathode in a galvanic cell. In solution, the anions move toward the anode and the cations move toward the cathode.
- The quantity of electricity carried by 1 mole of electrons is called a faraday, which is equal to 96,500 C.
- Standard reduction potentials show the relative likelihood of half-cell reduction reactions and can be used to predict the products, direction, and spontaneity of redox reactions between various substances.
- The decrease in free energy of the system in a spontaneous redox reaction is equal to the electrical work done by the system on the surroundings, or  $\Delta G = -nFE$ .
- The equilibrium constant for a redox reaction can be found from the standard electromotive force of a cell.
- The Nernst equation gives the relationship between the cell emf and the concentrations of the reactants and products under nonstandard-state conditions.
- Batteries, which consist of one or more galvanic cells, are used widely as self-contained power sources. Some of the better-known batteries are the dry cell, such as the Leclanché cell, the mercury battery, the lithium-ion battery, and the lead storage battery used in automobiles. Fuel cells produce electrical energy from a continuous supply of reactants.
- The corrosion of metals, such as the rusting of iron, is an electrochemical phenomenon.
- Electric current from an external source is used to drive a nonspontaneous chemical reaction in an electrolytic cell. The amount of product formed or reactant consumed depends on the quantity of electricity transferred at the electrode.
- Electrolysis plays an important role in obtaining pure metals from their ores and in purifying metals.

## KEY WORDS

Anode, p. 647  
 Battery, p. 661  
 Cathode, p. 647  
 Cell voltage, p. 647  
 Corrosion, p. 665

Electrochemistry, p. 643  
 Electrolysis, p. 668  
 Electrolytic cell, p. 668  
 Electromotive force (emf) ( $E$ ), p. 647

Faraday constant, p. 654  
 Fuel cell, p. 664  
 Galvanic cell, p. 646  
 Half-cell reaction, p. 647  
 Nernst equation, p. 657

Overvoltage, p. 670  
 Standard emf ( $E^\circ$ ), p. 649  
 Standard reduction potential, p. 648

## QUESTIONS AND PROBLEMS

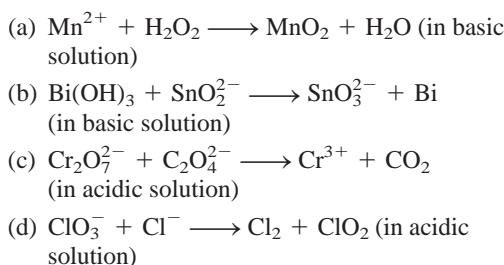
### Balancing Redox Equations

#### Problems

- 19.1 Balance the following redox equations by the half-reaction method:
- (a)  $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{H}_2\text{O}$  (in acidic solution)

- (b)  $\text{Cu} + \text{HNO}_3 \longrightarrow \text{Cu}^{2+} + \text{NO} + \text{H}_2\text{O}$  (in acidic solution)  
 (c)  $\text{CN}^- + \text{MnO}_4^- \longrightarrow \text{CNO}^- + \text{MnO}_2$  (in basic solution)  
 (d)  $\text{Br}_2 \longrightarrow \text{BrO}_3^- + \text{Br}^-$  (in basic solution)  
 (e)  $\text{S}_2\text{O}_3^{2-} + \text{I}_2 \longrightarrow \text{I}^- + \text{S}_4\text{O}_6^{2-}$  (in acidic solution)

- 19.2** Balance the following redox equations by the half-reaction method:



## Galvanic Cells and Standard Emfs

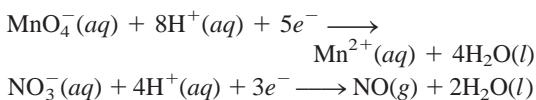
### Review Questions

- Define the following terms: anode, cathode, cell voltage, electromotive force, standard reduction potential.
- Describe the basic features of a galvanic cell. Why are the two components of the cell separated from each other?
- What is the function of a salt bridge? What kind of electrolyte should be used in a salt bridge?
- What is a cell diagram? Write the cell diagram for a galvanic cell consisting of an Al electrode placed in a 1 M  $\text{Al}(\text{NO}_3)_3$  solution and a Ag electrode placed in a 1 M  $\text{AgNO}_3$  solution.
- What is the difference between the half-reactions discussed in redox processes in Chapter 4 and the half-cell reactions discussed in Section 19.2?
- After operating a Daniell cell (see Figure 19.1) for a few minutes, a student notices that the cell emf begins to drop. Why?
- Use the information in Table 2.1, and calculate the Faraday constant.
- Discuss the spontaneity of an electrochemical reaction in terms of its standard emf ( $E_{\text{cell}}^{\circ}$ ).

### Problems

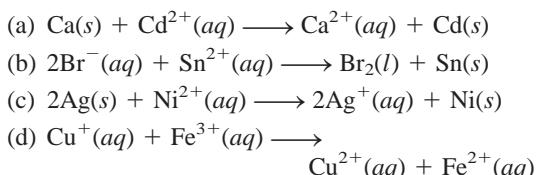
- Calculate the standard emf of a cell that uses the  $\text{Mg}/\text{Mg}^{2+}$  and  $\text{Cu}/\text{Cu}^{2+}$  half-cell reactions at 25°C. Write the equation for the cell reaction that occurs under standard-state conditions.
- Calculate the standard emf of a cell that uses  $\text{Ag}/\text{Ag}^+$  and  $\text{Al}/\text{Al}^{3+}$  half-cell reactions. Write the cell reaction that occurs under standard-state conditions.
- Predict whether  $\text{Fe}^{3+}$  can oxidize  $\text{I}^-$  to  $\text{I}_2$  under standard-state conditions.
- Which of the following reagents can oxidize  $\text{H}_2\text{O}$  to  $\text{O}_2(g)$  under standard-state conditions?  $\text{H}^+(aq)$ ,  $\text{Cl}^-(aq)$ ,  $\text{Cl}_2(g)$ ,  $\text{Cu}^{2+}(aq)$ ,  $\text{Pb}^{2+}(aq)$ ,  $\text{MnO}_4^-(aq)$  (in acid).

- 19.15** Consider the following half-reactions:



Predict whether  $\text{NO}_3^-$  ions will oxidize  $\text{Mn}^{2+}$  to  $\text{MnO}_4^-$  under standard-state conditions.

- 19.16** Predict whether the following reactions would occur spontaneously in aqueous solution at 25°C. Assume that the initial concentrations of dissolved species are all 1.0 M.



- 19.17** Which species in each pair is a better oxidizing agent under standard-state conditions? (a)  $\text{Br}_2$  or  $\text{Au}^{3+}$ , (b)  $\text{H}_2$  or  $\text{Ag}^+$ , (c)  $\text{Cd}^{2+}$  or  $\text{Cr}^{3+}$ , (d)  $\text{O}_2$  in acidic media or  $\text{O}_2$  in basic media.

- 19.18** Which species in each pair is a better reducing agent under standard-state conditions? (a)  $\text{Na}$  or  $\text{Li}$ , (b)  $\text{H}_2$  or  $\text{I}_2$ , (c)  $\text{Fe}^{2+}$  or  $\text{Ag}$ , (d)  $\text{Br}^-$  or  $\text{Co}^{2+}$ .

## Spontaneity of Redox Reactions

### Review Questions

- Write the equations relating  $\Delta G^\circ$  and  $K$  to the standard emf of a cell. Define all the terms.
- Compare the ease of measuring the equilibrium constant electrochemically with that by chemical means [see Equation (18.14)].

### Problems

- 19.21** What is the equilibrium constant for the following reaction at 25°C?

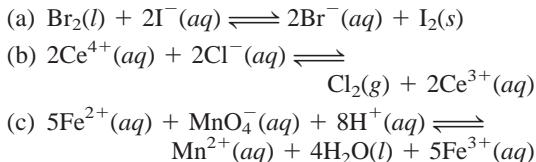


- 19.22** The equilibrium constant for the reaction

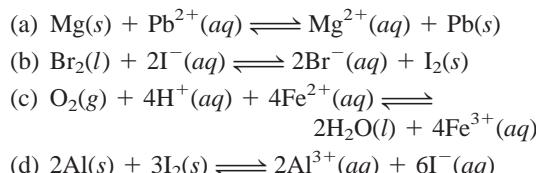


is  $2.69 \times 10^{12}$  at 25°C. Calculate  $E^\circ$  for a cell made up of  $\text{Sr}/\text{Sr}^{2+}$  and  $\text{Mg}/\text{Mg}^{2+}$  half-cells.

- 19.23** Use the standard reduction potentials to find the equilibrium constant for each of the following reactions at 25°C:



- 19.24** Calculate  $\Delta G^\circ$  and  $K_c$  for the following reactions at 25°C:



- 19.25** Under standard-state conditions, what spontaneous reaction will occur in aqueous solution among the ions  $Ce^{4+}$ ,  $Ce^{3+}$ ,  $Fe^{3+}$ , and  $Fe^{2+}$ ? Calculate  $\Delta G^\circ$  and  $K_c$  for the reaction.

- 19.26** Given that  $E^\circ = 0.52\text{ V}$  for the reduction  $Cu^+(aq) + e^- \rightarrow Cu(s)$ , calculate  $E^\circ$ ,  $\Delta G^\circ$ , and  $K$  for the following reaction at 25°C:



## The Effect of Concentration on Cell Emf

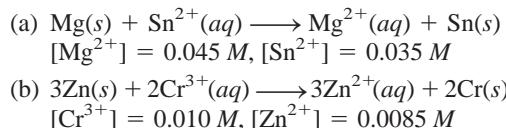
### Review Questions

- 19.27** Write the Nernst equation and explain all the terms.
- 19.28** Write the Nernst equation for the following processes at some temperature  $T$ :
- $Mg(s) + Sn^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Sn(s)$
  - $2Cr(s) + 3Pb^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Pb(s)$

### Problems

- 19.29** What is the potential of a cell made up of  $Zn/Zn^{2+}$  and  $Cu/Cu^{2+}$  half-cells at 25°C if  $[Zn^{2+}] = 0.25\text{ M}$  and  $[Cu^{2+}] = 0.15\text{ M}$ ?

- 19.30** Calculate  $E^\circ$ ,  $E$ , and  $\Delta G$  for the following cell reactions.



- 19.31** Calculate the standard potential of the cell consisting of the  $Zn/Zn^{2+}$  half-cell and the SHE. What will the emf of the cell be if  $[Zn^{2+}] = 0.45\text{ M}$ ,  $P_{H_2} = 2.0\text{ atm}$ , and  $[H^+] = 1.8\text{ M}$ ?

- 19.32** What is the emf of a cell consisting of a  $Pb^{2+}/Pb$  half-cell and a  $Pt/H^+/H_2$  half-cell if  $[Pb^{2+}] = 0.10\text{ M}$ ,  $[H^+] = 0.050\text{ M}$ , and  $P_{H_2} = 1.0\text{ atm}$ ?

- 19.33** Referring to the arrangement in Figure 19.1, calculate the  $[Cu^{2+}]/[Zn^{2+}]$  ratio at which the following reaction is spontaneous at 25°C:



- 19.34** Calculate the emf of the following concentration cell:



## Batteries and Fuel Cells

### Review Questions

- 19.35** Explain the differences between a primary galvanic cell—one that is not rechargeable—and a storage cell (for example, the lead storage battery), which is rechargeable.
- 19.36** Discuss the advantages and disadvantages of fuel cells over conventional power plants in producing electricity.

### Problems

- 19.37** The hydrogen-oxygen fuel cell is described in Section 19.6. (a) What volume of  $H_2(g)$ , stored at 25°C at a pressure of 155 atm, would be needed to run an electric motor drawing a current of 8.5 A for 3.0 h? (b) What volume (liters) of air at 25°C and 1.00 atm will have to pass into the cell per minute to run the motor? Assume that air is 20 percent  $O_2$  by volume and that all the  $O_2$  is consumed in the cell. The other components of air do not affect the fuel-cell reactions. Assume ideal gas behavior.

- 19.38** Calculate the standard emf of the propane fuel cell discussed on p. 665 at 25°C, given that  $\Delta G_f^\circ$  for propane is  $-23.5\text{ kJ/mol}$ .

## Corrosion

### Review Questions

- 19.39** Steel hardware, including nuts and bolts, is often coated with a thin plating of cadmium. Explain the function of the cadmium layer.
- 19.40** “Galvanized iron” is steel sheet that has been coated with zinc; “tin” cans are made of steel sheet coated with tin. Discuss the functions of these coatings and the electrochemistry of the corrosion reactions that occur if an electrolyte contacts the scratched surface of a galvanized iron sheet or a tin can.
- 19.41** Tarnished silver contains  $Ag_2S$ . The tarnish can be removed by placing silverware in an aluminum pan containing an inert electrolyte solution, such as NaCl. Explain the electrochemical principle for this procedure. [The standard reduction potential for the half-cell reaction  $Ag_2S(s) + 2e^- \rightarrow 2Ag(s) + S^{2-}(aq)$  is  $-0.71\text{ V}$ .]
- 19.42** How does the tendency of iron to rust depend on the pH of solution?

## Electrolysis

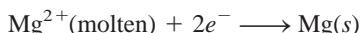
### Review Questions

- 19.43** What is the difference between a galvanic cell (such as a Daniell cell) and an electrolytic cell?

- 19.44 What is Faraday's contribution to quantitative electrolysis?

### Problems

- 19.45 The half-reaction at an electrode is

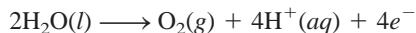


Calculate the number of grams of magnesium that can be produced by supplying  $1.00\text{ F}$  to the electrode.

- 19.46** Consider the electrolysis of molten barium chloride,  $\text{BaCl}_2$ . (a) Write the half-reactions. (b) How many grams of barium metal can be produced by supplying  $0.50\text{ A}$  for  $30\text{ min}$ ?
- 19.47 Considering only the cost of electricity, would it be cheaper to produce a ton of sodium or a ton of aluminum by electrolysis?

- 19.48** If the cost of electricity to produce magnesium by the electrolysis of molten magnesium chloride is \$155 per ton of metal, what is the cost (in dollars) of the electricity necessary to produce (a)  $10.0\text{ tons}$  of aluminum, (b)  $30.0\text{ tons}$  of sodium, (c)  $50.0\text{ tons}$  of calcium?

- 19.49 One of the half-reactions for the electrolysis of water is



If  $0.076\text{ L}$  of  $\text{O}_2$  is collected at  $25^\circ\text{C}$  and  $755\text{ mmHg}$ , how many faradays of electricity had to pass through the solution?

- 19.50** How many faradays of electricity are required to produce (a)  $0.84\text{ L}$  of  $\text{O}_2$  at exactly  $1\text{ atm}$  and  $25^\circ\text{C}$  from aqueous  $\text{H}_2\text{SO}_4$  solution; (b)  $1.50\text{ L}$  of  $\text{Cl}_2$  at  $750\text{ mmHg}$  and  $20^\circ\text{C}$  from molten  $\text{NaCl}$ ; (c)  $6.0\text{ g}$  of Sn from molten  $\text{SnCl}_2$ ?

- 19.51 Calculate the amounts of  $\text{Cu}$  and  $\text{Br}_2$  produced in  $1.0\text{ h}$  at inert electrodes in a solution of  $\text{CuBr}_2$  by a current of  $4.50\text{ A}$ .

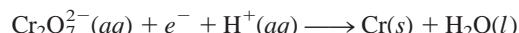
- 19.52** In the electrolysis of an aqueous  $\text{AgNO}_3$  solution,  $0.67\text{ g}$  of  $\text{Ag}$  is deposited after a certain period of time. (a) Write the half-reaction for the reduction of  $\text{Ag}^+$ . (b) What is the probable oxidation half-reaction? (c) Calculate the quantity of electricity used, in coulombs.

- 19.53 A steady current was passed through molten  $\text{CoSO}_4$  until  $2.35\text{ g}$  of metallic cobalt was produced. Calculate the number of coulombs of electricity used.

- 19.54** A constant electric current flows for  $3.75\text{ h}$  through two electrolytic cells connected in series. One contains a solution of  $\text{AgNO}_3$  and the second a solution of  $\text{CuCl}_2$ . During this time  $2.00\text{ g}$  of silver are deposited in the first cell. (a) How many grams of copper are deposited in the second cell? (b) What is the current flowing, in amperes?

- 19.55 What is the hourly production rate of chlorine gas (in kg) from an electrolytic cell using aqueous  $\text{NaCl}$  electrolyte and carrying a current of  $1.500 \times 10^3\text{ A}$ ? The anode efficiency for the oxidation of  $\text{Cl}^-$  is 93.0 percent.

- 19.56** Chromium plating is applied by electrolysis to objects suspended in a dichromate solution, according to the following (unbalanced) half-reaction:



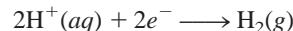
How long (in hours) would it take to apply a chromium plating  $1.0 \times 10^{-2}\text{ mm}$  thick to a car bumper with a surface area of  $0.25\text{ m}^2$  in an electrolytic cell carrying a current of  $25.0\text{ A}$ ? (The density of chromium is  $7.19\text{ g/cm}^3$ .)

- 19.57 The passage of a current of  $0.750\text{ A}$  for  $25.0\text{ min}$  deposited  $0.369\text{ g}$  of copper from a  $\text{CuSO}_4$  solution. From this information, calculate the molar mass of copper.

- 19.58** A quantity of  $0.300\text{ g}$  of copper was deposited from a  $\text{CuSO}_4$  solution by passing a current of  $3.00\text{ A}$  through the solution for  $304\text{ s}$ . Calculate the value of the faraday constant.

- 19.59 In a certain electrolysis experiment,  $1.44\text{ g}$  of  $\text{Ag}$  were deposited in one cell (containing an aqueous  $\text{AgNO}_3$  solution), while  $0.120\text{ g}$  of an unknown metal X was deposited in another cell (containing an aqueous  $\text{XCl}_3$  solution) in series with the  $\text{AgNO}_3$  cell. Calculate the molar mass of X.

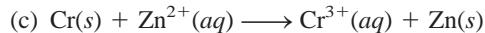
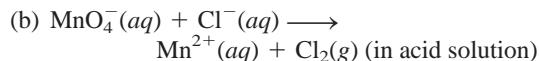
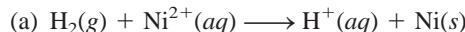
- 19.60** One of the half-reactions for the electrolysis of water is



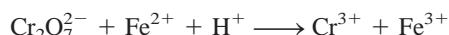
If  $0.845\text{ L}$  of  $\text{H}_2$  is collected at  $25^\circ\text{C}$  and  $782\text{ mmHg}$ , how many faradays of electricity had to pass through the solution?

### Additional Problems

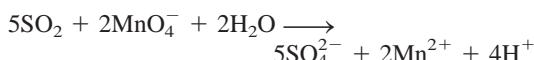
- 19.61 For each of the following redox reactions, (i) write the half-reactions; (ii) write a balanced equation for the whole reaction, (iii) determine in which direction the reaction will proceed spontaneously under standard-state conditions:



- 19.62** The oxidation of  $25.0\text{ mL}$  of a solution containing  $\text{Fe}^{2+}$  requires  $26.0\text{ mL}$  of  $0.0250\text{ M}$   $\text{K}_2\text{Cr}_2\text{O}_7$  in acidic solution. Balance the following equation and calculate the molar concentration of  $\text{Fe}^{2+}$ :



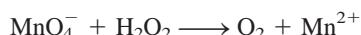
- 19.63 The  $\text{SO}_2$  present in air is mainly responsible for the phenomenon of acid rain. The concentration of  $\text{SO}_2$  can be determined by titrating against a standard permanganate solution as follows:



Calculate the number of grams of  $\text{SO}_2$  in a sample of air if 7.37 mL of 0.00800 M  $\text{KMnO}_4$  solution are required for the titration.

- 19.64 A sample of iron ore weighing 0.2792 g was dissolved in an excess of a dilute acid solution. All the iron was first converted to  $\text{Fe}(\text{II})$  ions. The solution then required 23.30 mL of 0.0194 M  $\text{KMnO}_4$  for oxidation to  $\text{Fe}(\text{III})$  ions. Calculate the percent by mass of iron in the ore.

- 19.65 The concentration of a hydrogen peroxide solution can be conveniently determined by titration against a standardized potassium permanganate solution in an acidic medium according to the following unbalanced equation:



(a) Balance the above equation. (b) If 36.44 mL of a 0.01652 M  $\text{KMnO}_4$  solution are required to completely oxidize 25.00 mL of a  $\text{H}_2\text{O}_2$  solution, calculate the molarity of the  $\text{H}_2\text{O}_2$  solution.

- 19.66 Oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) is present in many plants and vegetables. (a) Balance the following equation in acid solution:



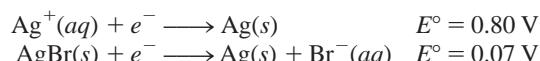
(b) If a 1.00-g sample of  $\text{H}_2\text{C}_2\text{O}_4$  requires 24.0 mL of 0.0100 M  $\text{KMnO}_4$  solution to reach the equivalence point, what is the percent by mass of  $\text{H}_2\text{C}_2\text{O}_4$  in the sample?

- 19.67 Complete the following table. State whether the cell reaction is spontaneous, nonspontaneous, or at equilibrium.

| $E$   | $\Delta G$ | Cell Reaction |
|-------|------------|---------------|
| $> 0$ |            |               |
|       | $> 0$      |               |
| $= 0$ |            |               |

- 19.68 Calcium oxalate ( $\text{CaC}_2\text{O}_4$ ) is insoluble in water. This property has been used to determine the amount of  $\text{Ca}^{2+}$  ions in blood. The calcium oxalate isolated from blood is dissolved in acid and titrated against a standardized  $\text{KMnO}_4$  solution, as described in Problem 19.66. In one test it is found that the calcium oxalate isolated from a 10.0-mL sample of blood requires 24.2 mL of  $9.56 \times 10^{-4}$  M  $\text{KMnO}_4$  for titration. Calculate the number of milligrams of calcium per milliliter of blood.

- 19.69 From the following information, calculate the solubility product of  $\text{AgBr}$ :



- 19.70 Consider a galvanic cell composed of the SHE and a half-cell using the reaction  $\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$ .

(a) Calculate the standard cell potential. (b) What is the spontaneous cell reaction under standard-state conditions? (c) Calculate the cell potential when  $[\text{H}^+]$  in the hydrogen electrode is changed to (i)  $1.0 \times 10^{-2}$  M and (ii)  $1.0 \times 10^{-5}$  M, all other reagents being held at standard-state conditions. (d) Based on this cell arrangement, suggest a design for a pH meter.

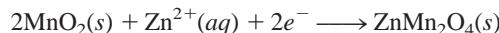
- 19.71 A galvanic cell consists of a silver electrode in contact with 346 mL of 0.100 M  $\text{AgNO}_3$  solution and a magnesium electrode in contact with 288 mL of 0.100 M  $\text{Mg}(\text{NO}_3)_2$  solution. (a) Calculate  $E$  for the cell at 25°C. (b) A current is drawn from the cell until 1.20 g of silver have been deposited at the silver electrode. Calculate  $E$  for the cell at this stage of operation.

- 19.72 Explain why chlorine gas can be prepared by electrolyzing an aqueous solution of  $\text{NaCl}$  but fluorine gas cannot be prepared by electrolyzing an aqueous solution of  $\text{NaF}$ .

- 19.73 Calculate the emf of the following concentration cell at 25°C:



- 19.74 The cathode reaction in the Leclanché cell is given by



If a Leclanché cell produces a current of 0.0050 A, calculate how many hours this current supply will last if there are initially 4.0 g of  $\text{MnO}_2$  present in the cell. Assume that there is an excess of  $\text{Zn}^{2+}$  ions.

- 19.75 Suppose you are asked to verify experimentally the electrode reactions shown in Example 19.8. In addition to the apparatus and the solution, you are also given two pieces of litmus paper, one blue and the other red. Describe what steps you would take in this experiment.

- 19.76 For a number of years it was not clear whether mercury(I) ions existed in solution as  $\text{Hg}^+$  or as  $\text{Hg}_2^{2+}$ . To distinguish between these two possibilities, we could set up the following system:



where soln A contained 0.263 g mercury(I) nitrate per liter and soln B contained 2.63 g mercury(I) nitrate per liter. If the measured emf of such a cell is 0.0289 V at 18°C, what can you deduce about the nature of the mercury(I) ions?

- 19.77 An aqueous KI solution to which a few drops of phenolphthalein have been added is electrolyzed using an apparatus like the one shown here:



Describe what you would observe at the anode and the cathode. (*Hint:* Molecular iodine is only slightly soluble in water, but in the presence of  $I^-$  ions, it forms the brown color of  $I_3^-$  ions.)

- 19.78 A piece of magnesium metal weighing 1.56 g is placed in 100.0 mL of 0.100 M  $AgNO_3$  at 25°C. Calculate  $[Mg^{2+}]$  and  $[Ag^+]$  in solution at equilibrium. What is the mass of the magnesium left? The volume remains constant.

- 19.79 Describe an experiment that would enable you to determine which is the cathode and which is the anode in a galvanic cell using copper and zinc electrodes.

- 19.80 An acidified solution was electrolyzed using copper electrodes. A constant current of 1.18 A caused the anode to lose 0.584 g after  $1.52 \times 10^3$  s. (a) What is the gas produced at the cathode and what is its volume at STP? (b) Given that the charge of an electron is  $1.6022 \times 10^{-19}$  C, calculate Avogadro's number. Assume that copper is oxidized to  $Cu^{2+}$  ions.

- 19.81 In a certain electrolysis experiment involving  $Al^{3+}$  ions, 60.2 g of Al is recovered when a current of 0.352 A is used. How many minutes did the electrolysis last?

- 19.82 Consider the oxidation of ammonia:



(a) Calculate the  $\Delta G^\circ$  for the reaction. (b) If this reaction were used in a fuel cell, what would the standard cell potential be?

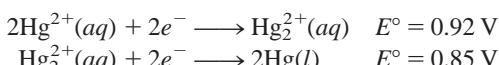
- 19.83 A galvanic cell is constructed by immersing a piece of copper wire in 25.0 mL of a 0.20 M  $CuSO_4$  solution and a zinc strip in 25.0 mL of a 0.20 M  $ZnSO_4$  solution. (a) Calculate the emf of the cell at 25°C and predict what would happen if a small amount of concentrated  $NH_3$  solution were added to (i) the  $CuSO_4$  solution and (ii) the  $ZnSO_4$  solution. Assume that the volume in each compartment remains constant at

25.0 mL. (b) In a separate experiment, 25.0 mL of 3.00 M  $NH_3$  are added to the  $CuSO_4$  solution. If the emf of the cell is 0.68 V, calculate the formation constant ( $K_f$ ) of  $Cu(NH_3)_2^{2+}$ .

- 19.84 In an electrolysis experiment, a student passes the same quantity of electricity through two electrolytic cells, one containing a silver salt and the other a gold salt. Over a certain period of time, she finds that 2.64 g of Ag and 1.61 g of Au are deposited at the cathodes. What is the oxidation state of gold in the gold salt?

- 19.85 People living in cold-climate countries where there is plenty of snow are advised not to heat their garages in the winter. What is the electrochemical basis for this recommendation?

- 19.86 Given that



calculate  $\Delta G^\circ$  and  $K$  for the following process at 25°C:



(The preceding reaction is an example of a *disproportionation reaction* in which an element in one oxidation state is both oxidized and reduced.)

- 19.87 Fluorine ( $F_2$ ) is obtained by the electrolysis of liquid hydrogen fluoride (HF) containing potassium fluoride (KF). (a) Write the half-cell reactions and the overall reaction for the process. (b) What is the purpose of KF? (c) Calculate the volume of  $F_2$  (in liters) collected at 24.0°C and 1.2 atm after electrolyzing the solution for 15 h at a current of 502 A.

- 19.88 A 300-mL solution of NaCl was electrolyzed for 6.00 min. If the pH of the final solution was 12.24, calculate the average current used.

- 19.89 Industrially, copper is purified by electrolysis. The impure copper acts as the anode, and the cathode is made of pure copper. The electrodes are immersed in a  $CuSO_4$  solution. During electrolysis, copper at the anode enters the solution as  $Cu^{2+}$  while  $Cu^{2+}$  ions are reduced at the cathode. (a) Write half-cell reactions and the overall reaction for the electrolytic process. (b) Suppose the anode was contaminated with Zn and Ag. Explain what happens to these impurities during electrolysis. (c) How many hours will it take to obtain 1.00 kg of Cu at a current of 18.9 A?

- 19.90 An aqueous solution of a platinum salt is electrolyzed at a current of 2.50 A for 2.00 h. As a result, 9.09 g of metallic Pt are formed at the cathode. Calculate the charge on the Pt ions in this solution.

- 19.91 Consider a galvanic cell consisting of a magnesium electrode in contact with 1.0 M  $Mg(NO_3)_2$  and a cadmium electrode in contact with 1.0 M  $Cd(NO_3)_2$ . Calculate  $E^\circ$  for the cell, and draw a diagram showing the cathode, anode, and direction of electron flow.

**19.92** A current of 6.00 A passes through an electrolytic cell containing dilute sulfuric acid for 3.40 h. If the volume of O<sub>2</sub> gas generated at the anode is 4.26 L (at STP), calculate the charge (in coulombs) on an electron.

**19.93** Gold will not dissolve in either concentrated nitric acid or concentrated hydrochloric acid. However, the metal does dissolve in a mixture of the acids (one part HNO<sub>3</sub> and three parts HCl by volume), called *aqua regia*. (a) Write a balanced equation for this reaction. (*Hint:* Among the products are HAuCl<sub>4</sub> and NO<sub>2</sub>.) (b) What is the function of HCl?

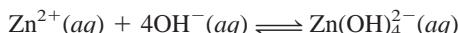
**19.94** Explain why most useful galvanic cells give voltages of no more than 1.5 to 2.5 V. What are the prospects for developing practical galvanic cells with voltages of 5 V or more?

**19.95** A silver rod and a SHE are dipped into a saturated aqueous solution of silver oxalate, Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, at 25°C. The measured potential difference between the rod and the SHE is 0.589 V, the rod being positive. Calculate the solubility product constant for silver oxalate.

**19.96** Zinc is an amphoteric metal; that is, it reacts with both acids and bases. The standard reduction potential is −1.36 V for the reaction

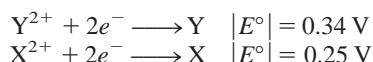


Calculate the formation constant ( $K_f$ ) for the reaction



**19.97** Use the data in Table 19.1 to determine whether or not hydrogen peroxide will undergo disproportionation in an acid medium: 2H<sub>2</sub>O<sub>2</sub> → 2H<sub>2</sub>O + O<sub>2</sub>.

**19.98** The magnitudes (but *not* the signs) of the standard reduction potentials of two metals X and Y are



where the || notation denotes that only the magnitude (but not the sign) of the  $E^\circ$  value is shown. When the half-cells of X and Y are connected, electrons flow from X to Y. When X is connected to a SHE, electrons flow from X to SHE. (a) Are the  $E^\circ$  values of the half-reactions positive or negative? (b) What is the standard emf of a cell made up of X and Y?

**19.99** A galvanic cell is constructed as follows. One half-cell consists of a platinum wire immersed in a solution containing 1.0 M Sn<sup>2+</sup> and 1.0 M Sn<sup>4+</sup>; the other half-cell has a thallium rod immersed in a solution of 1.0 M Tl<sup>+</sup>. (a) Write the half-cell reactions and the overall reaction. (b) What is the equilibrium constant at 25°C? (c) What is the cell voltage if the Tl<sup>+</sup> concentration is increased tenfold? ( $E_{\text{Tl}^+/\text{Tl}}^\circ = -0.34 \text{ V}$ .)

**19.100** Given the standard reduction potential for Au<sup>3+</sup> in Table 19.1 and



answer the following questions. (a) Why does gold not tarnish in air? (b) Will the following disproportionation occur spontaneously?



(c) Predict the reaction between gold and fluorine gas.

**19.101** Calculate  $E^\circ$  for the reactions of mercury with (a) 1 M HCl and (b) 1 M HNO<sub>3</sub>. Which acid will oxidize Hg to Hg<sup>2+</sup> under standard-state conditions? Can you identify which test tube below contains HNO<sub>3</sub> and Hg and which contains HCl and Hg?



Based on your answer, explain why ingestion of a very small quantity of mercury is not considered too harmful.

**19.102** When 25.0 mL of a solution containing both Fe<sup>2+</sup> and Fe<sup>3+</sup> ions is titrated with 23.0 mL of 0.0200 M KMnO<sub>4</sub> (in dilute sulfuric acid), all of the Fe<sup>2+</sup> ions are oxidized to Fe<sup>3+</sup> ions. Next, the solution is treated with Zn metal to convert all of the Fe<sup>3+</sup> ions to Fe<sup>2+</sup> ions. Finally, 40.0 mL of the same KMnO<sub>4</sub> solution are added to the solution in order to oxidize the Fe<sup>2+</sup> ions to Fe<sup>3+</sup>. Calculate the molar concentrations of Fe<sup>2+</sup> and Fe<sup>3+</sup> in the original solution.

**19.103** Consider the Daniell cell in Figure 19.1. When viewed externally, the anode appears negative and the cathode positive (electrons are flowing from the anode to the cathode). Yet in solution anions are moving toward the anode, which means that it must appear positive to the anions. Because the anode cannot simultaneously be negative and positive, give an explanation for this apparently contradictory situation.

**19.104** Lead storage batteries are rated by ampere hours, that is, the number of amperes they can deliver in an hour. (a) Show that 1 A · h = 3600 C. (b) The lead anodes of a certain lead storage battery have a total mass of 406 g. Calculate the maximum theoretical capacity of the battery in ampere hours. Explain why in practice we can never extract this much energy from the battery. (*Hint:* Assume all of the lead will be used up in the electrochemical reaction and refer to the electrode reactions on p. 662.) (c) Calculate  $E_{\text{cell}}^\circ$  and  $\Delta G^\circ$  for the battery.

**19.105** The concentration of sulfuric acid in the lead storage battery of an automobile over a period of time has

decreased from 38.0 percent by mass (density = 1.29 g/mL) to 26.0 percent by mass (1.19 g/mL). Assume the volume of the acid remains constant at 724 mL. (a) Calculate the total charge in coulombs supplied by the battery. (b) How long (in hours) will it take to recharge the battery back to the original sulfuric acid concentration using a current of 22.4 A.

- 19.106** Consider a Daniell cell operating under nonstandard-state conditions. Suppose that the cell's reaction is multiplied by 2. What effect does this have on each of the following quantities in the Nernst equation? (a)  $E$ , (b)  $E^\circ$ , (c)  $Q$ , (d)  $\ln Q$ , and (e)  $n$ ?

- 19.107** A spoon was silver-plated electrolytically in a  $\text{AgNO}_3$  solution. (a) Sketch a diagram for the process. (b) If 0.884 g of Ag was deposited on the spoon at a constant current of 18.5 mA, how long (in minutes) did the electrolysis take?

- 19.108** Comment on whether  $\text{F}_2$  will become a stronger oxidizing agent with increasing  $\text{H}^+$  concentration.

- 19.109** In recent years there has been much interest in electric cars. List some advantages and disadvantages of electric cars compared to automobiles with internal combustion engines.

- 19.110** Calculate the pressure of  $\text{H}_2$  (in atm) required to maintain equilibrium with respect to the following reaction at  $25^\circ\text{C}$ :



Given that  $[\text{Pb}^{2+}] = 0.035\text{ M}$  and the solution is buffered at pH 1.60.

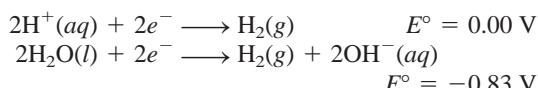
- 19.111** Because all alkali metals react with water, it is not possible to measure the standard reduction potentials of these metals directly as in the case of, say, zinc. An indirect method is to consider the following hypothetical reaction



Use the appropriate equation presented in this chapter and the thermodynamic data in Appendix 2, calculate  $E^\circ$  for  $\text{Li}^+(aq) + e^- \rightarrow \text{Li}(s)$  at  $298\text{ K}$ . Compare your result with that listed in Table 19.1. (See back endpaper for the Faraday constant.)

- 19.112** A galvanic cell using  $\text{Mg}/\text{Mg}^{2+}$  and  $\text{Cu}/\text{Cu}^{2+}$  half-cells operates under standard-state conditions at  $25^\circ\text{C}$  and each compartment has a volume of 218 mL. The cell delivers 0.22 A for 31.6 h. (a) How many grams of Cu are deposited? (b) What is the  $[\text{Cu}^{2+}]$  remaining?

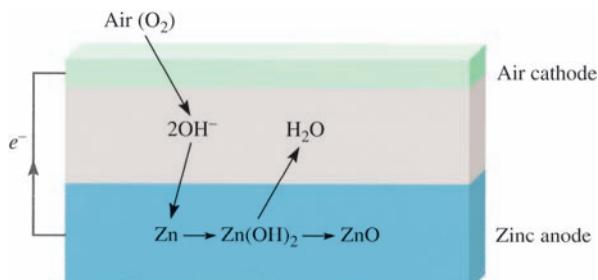
- 19.113** Given the following standard reduction potentials, calculate the ion-product,  $K_w$ , for water at  $25^\circ\text{C}$ :



## SPECIAL PROBLEMS

- 19.114** A piece of magnesium ribbon and a copper wire are partially immersed in a  $0.1\text{ M HCl}$  solution in a beaker. The metals are joined externally by another piece of metal wire. Bubbles are seen to evolve at both the Mg and Cu surfaces. (a) Write equations representing the reactions occurring at the metals. (b) What visual evidence would you seek to show that Cu is not oxidized to  $\text{Cu}^{2+}$ ? (c) At some stage, NaOH solution is added to the beaker to neutralize the HCl acid. Upon further addition of NaOH, a white precipitate forms. What is it?

- 19.115** The zinc-air battery shows much promise for electric cars because it is lightweight and rechargeable:



The net transformation is  $\text{Zn}(s) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{ZnO}(s)$

(a) Write the half-reactions at the zinc-air electrodes and calculate the standard emf of the battery at  $25^\circ\text{C}$ .  
 (b) Calculate the emf under actual operating conditions when the partial pressure of oxygen is 0.21 atm. (c) What is the energy density (measured as the energy in kilojoules that can be obtained from 1 kg of the metal) of the zinc electrode? (d) If a current of  $2.1 \times 10^5\text{ A}$  is to be drawn from a zinc-air battery system, what volume of air (in liters) would need to be supplied to the battery every second? Assume that the temperature is  $25^\circ\text{C}$  and the partial pressure of oxygen is 0.21 atm.

- 19.116** Calculate the equilibrium constant for the following reaction at  $298\text{ K}$ :



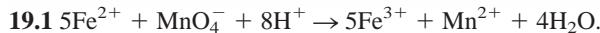
- 19.117** A construction company is installing an iron culvert (a long cylindrical tube) that is 40.0 m long with a radius of 0.900 m. To prevent corrosion, the culvert must be galvanized. This process is carried out by first passing an iron sheet of appropriate dimensions through an electrolytic cell containing  $\text{Zn}^{2+}$  ions, using graphite as the anode and the iron sheet as the

cathode. If the voltage is 3.26 V, what is the cost of electricity for depositing a layer 0.200 mm thick if the efficiency of the process is 95 percent? The electricity rate is \$0.12 per kilowatt hour (kWh), where 1 W = 1 J/s and the density of Zn is 7.14 g/cm<sup>3</sup>.

- 19.118** A  $9.00 \times 10^2$ -mL 0.200 M MgI<sub>2</sub> was electrolyzed. As a result, hydrogen gas was generated at the cathode and iodine was formed at the anode. The volume of hydrogen collected at 26°C and 779 mmHg was  $1.22 \times 10^3$  mL. (a) Calculate the charge in coulombs consumed in the process. (b) How long (in min) did the electrolysis last if a current of 7.55 A was used? (c) A white precipitate was formed in the process. What was it and what was its mass in grams? Assume the volume of the solution was constant.
- 19.119** To remove the tarnish (Ag<sub>2</sub>S) on a silver spoon, a student carried out the following steps. First, she placed the spoon in a large pan filled with water so the spoon

was totally immersed. Next, she added a few tablespoonfuls of baking soda (sodium bicarbonate), which readily dissolved. Finally, she placed some aluminum foil at the bottom of the pan in contact with the spoon and then heated the solution to about 80°C. After a few minutes, the spoon was removed and rinsed with cold water. The tarnish was gone and the spoon regained its original shiny appearance. (a) Describe with equations the electrochemical basis for the procedure. (b) Adding NaCl instead of NaHCO<sub>3</sub> would also work because both compounds are strong electrolytes. What is the added advantage of using NaHCO<sub>3</sub>? (*Hint:* Consider the pH of the solution.) (c) What is the purpose of heating the solution? (d) Some commercial tarnish removers containing a fluid (or paste) that is a dilute HCl solution. Rubbing the spoon with the fluid will also remove the tarnish. Name two disadvantages of using this procedure compared to the one described here.

## ANSWERS TO PRACTICE EXERCISES

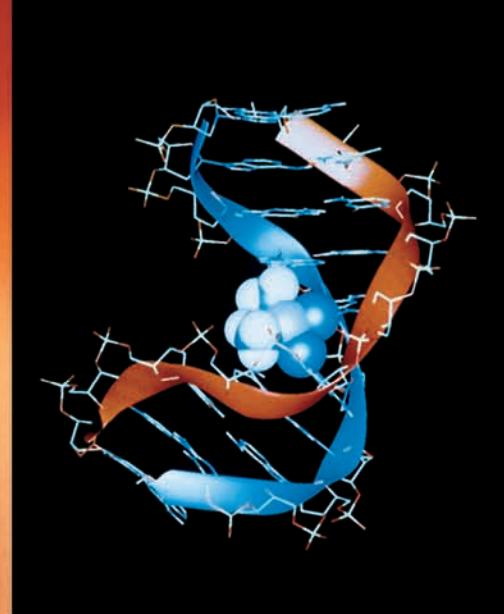


**19.2** No. **19.3** 0.34 V. **19.4**  $1 \times 10^{-42}$ .

**19.5**  $\Delta G^\circ = -4.1 \times 10^2$  kJ/mol. **19.6** Yes,  $E = +0.01$  V.

**19.7** 0.38 V. **19.8** Anode, O<sub>2</sub>; cathode, H<sub>2</sub>.

**19.9**  $2.0 \times 10^4$  A.



Cisplatin disrupts DNA replication and transcription by binding to the double helix. The structure of this major DNA adduct, depicted here, was elucidated by Professor Stephen Lippard's group at MIT.

## The Chemistry of Coordination Compounds

### CHAPTER OUTLINE

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Hemoglobin and Related Compounds • Cisplatin

### ESSENTIAL CONCEPTS

**Coordination Compounds** A coordination compound contains one or more complex ions in which a small number of molecules or ions surround a central metal atom or ion, usually of the transition metal family. Common geometries of coordination compounds are linear, tetrahedral, square planar, and octahedral.

**Bonding in Coordination Compounds** Crystal field theory explains the bonding in a complex ion in terms of electrostatic forces. The approach of the ligands toward the metal causes a splitting in energy in the five  $d$  orbitals. The extent of the splitting, called crystal-field splitting, depends on the nature of the ligands. Crystal field theory successfully accounts for the color and magnetic properties of many complex ions.

**Coordination Compounds in Living Systems** Coordination compounds play many important roles in animals and plants. They are also used as therapeutic drugs.



### Activity Summary

1. Animation: Absorption of Color (20.4)

## 20.1 Properties of the Transition Metals

Transition metals typically have incompletely filled *d* subshells or readily give rise to ions with incompletely filled *d* subshells (Figure 20.1). (The Group 2B metals—Zn, Cd, and Hg—do not have this characteristic electron configuration and so, although they are sometimes called transition metals, they really do not belong in this category.) This attribute is responsible for several notable properties, including distinctive coloring, formation of paramagnetic compounds, catalytic activity, and especially a great tendency to form complex ions. In this chapter we focus on the first-row elements from scandium to copper, the most common transition metals (Figure 20.2). Table 20.1 lists some of their properties.

As we read across any period from left to right, atomic numbers increase, electrons are added to the outer shell, and the nuclear charge increases by the addition of protons. In the third-period elements—sodium to argon—the outer electrons weakly shield one another from the extra nuclear charge. Consequently, atomic radii decrease rapidly from sodium to argon, and the electronegativities and ionization energies increase steadily (see Figures 8.5, 8.9, and 9.5).

For the transition metals, the trends are different. Looking at Table 20.1 we see that the nuclear charge, of course, increases from scandium to copper, but electrons are being added to the inner *3d* subshell. These *3d* electrons shield the *4s* electrons from the increasing nuclear charge somewhat more effectively than outer-shell electrons can shield one another, so the atomic radii decrease less rapidly. For the same reason, electronegativities and ionization energies increase only slightly from scandium across to copper compared with the increases from sodium to argon.

Although the transition metals are less electropositive (or more electronegative) than the alkali and alkaline earth metals, their standard reduction potentials suggest that all of them except copper should react with strong acids such as hydrochloric acid to produce hydrogen gas. However, most transition metals are inert toward acids or react slowly with them because of a protective layer of oxide. A case in point is

| 1<br>1A  |          |          |           |           |           |           |           |           |           |           |          |          | 18<br>8A |          |          |          |          |
|----------|----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|----------|----------|----------|----------|----------|----------|
| 1<br>H   | 2<br>2A  |          |           |           |           |           |           |           |           |           |          |          |          | 2<br>He  |          |          |          |
| 3<br>Li  | 4<br>Be  |          |           |           |           |           |           |           |           |           |          |          |          | 5<br>B   |          |          |          |
| 11<br>Na | 12<br>Mg | 3<br>3B  | 4<br>4B   | 5<br>5B   | 6<br>6B   | 7<br>7B   | 8         | 9         | 10        | 11<br>1B  | 12<br>2B | 13<br>Al | 14<br>Si | 15<br>P  | 16<br>S  | 17<br>Cl | 18<br>Ar |
| 19<br>K  | 20<br>Ca | 21<br>Sc | 22<br>Ti  | 23<br>V   | 24<br>Cr  | 25<br>Mn  | 26<br>Fe  | 27<br>Co  | 28<br>Ni  | 29<br>Cu  | 30<br>Zn | 31<br>Ga | 32<br>Ge | 33<br>As | 34<br>Se | 35<br>Br | 36<br>Kr |
| 37<br>Rb | 38<br>Sr | 39<br>Y  | 40<br>Zr  | 41<br>Nb  | 42<br>Mo  | 43<br>Tc  | 44<br>Ru  | 45<br>Rh  | 46<br>Pd  | 47<br>Ag  | 48<br>Cd | 49<br>In | 50<br>Sn | 51<br>Sb | 52<br>Te | 53<br>I  | 54<br>Xe |
| 55<br>Cs | 56<br>Ba | 57<br>La | 72<br>Hf  | 73<br>Ta  | 74<br>W   | 75<br>Re  | 76<br>Os  | 77<br>Ir  | 78<br>Pt  | 79<br>Au  | 80<br>Hg | 81<br>Tl | 82<br>Pb | 83<br>Bi | 84<br>Po | 85<br>At | 86<br>Rn |
| 87<br>Fr | 88<br>Ra | 89<br>Ac | 104<br>Rf | 105<br>Db | 106<br>Sg | 107<br>Bh | 108<br>Hs | 109<br>Mt | 110<br>Ds | 111<br>Rg | 112      | (113)    | 114      | (115)    | 116      | (117)    | (118)    |

**Figure 20.1**

The transition metals (blue squares). Note that although the Group 2B elements (Zn, Cd, Hg) are described as transition metals by some chemists, neither the metals nor their ions possess incompletely filled *d* subshells.



Scandium (Sc)



Titanium (Ti)



Vanadium (V)



Chromium (Cr)



Manganese (Mn)



Iron (Fe)



Cobalt (Co)



Nickel (Ni)



Copper (Cu)

**Figure 20.2***The first-row transition metals.*

chromium: Despite a rather negative standard reduction potential, it is quite inert chemically because of the formation on its surfaces of chromium(III) oxide,  $\text{Cr}_2\text{O}_3$ . Consequently, chromium is commonly used as a protective and noncorrosive plating on other metals. On automobile bumpers and trim, chromium plating serves a decorative as well as a functional purpose.

## Electron Configurations

The electron configurations of the first-row transition metals were discussed in Section 7.9. Calcium has the electron configuration  $[\text{Ar}]4s^2$ . From scandium across to copper, electrons are added to the  $3d$  orbitals. Thus, the outer electron configuration of scandium is  $4s^23d^1$ , that of titanium is  $4s^23d^2$ , and so on. The two exceptions are chromium and copper, whose outer electron configurations are  $4s^13d^5$  and  $4s^13d^{10}$ , respectively. These irregularities are the result of the extra stability associated with half-filled and completely filled  $3d$  subshells.

When the first-row transition metals form cations, electrons are removed first from the  $4s$  orbitals and then from the  $3d$  orbitals. (This is the opposite of the order in which orbitals are filled in neutral atoms.) For example, the outer electron configuration of  $\text{Fe}^{2+}$  is  $3d^6$ , not  $4s^23d^4$ .

**TABLE 20.1** Electron Configurations and Other Properties of the First-Row Transition Metals

|                                   | Sc         | Ti         | V          | Cr         | Mn         | Fe         | Co         | Ni         | Cu            |
|-----------------------------------|------------|------------|------------|------------|------------|------------|------------|------------|---------------|
| Electron configuration            |            |            |            |            |            |            |            |            |               |
| M                                 | $4s^23d^1$ | $4s^23d^2$ | $4s^23d^3$ | $4s^13d^5$ | $4s^23d^5$ | $4s^23d^6$ | $4s^23d^7$ | $4s^23d^8$ | $4s^13d^{10}$ |
| $M^{2+}$                          | —          | $3d^2$     | $3d^3$     | $3d^4$     | $3d^5$     | $3d^6$     | $3d^7$     | $3d^8$     | $3d^9$        |
| $M^{3+}$                          | [Ar]       | $3d^1$     | $3d^2$     | $3d^3$     | $3d^4$     | $3d^5$     | $3d^6$     | $3d^7$     | $3d^8$        |
| Electronegativity                 | 1.3        | 1.5        | 1.6        | 1.6        | 1.5        | 1.8        | 1.9        | 1.9        | 1.9           |
| Ionization energy<br>(kJ/mol)     |            |            |            |            |            |            |            |            |               |
| First                             | 631        | 658        | 650        | 652        | 717        | 759        | 760        | 736        | 745           |
| Second                            | 1235       | 1309       | 1413       | 1591       | 1509       | 1561       | 1645       | 1751       | 1958          |
| Third                             | 2389       | 2650       | 2828       | 2986       | 3250       | 2956       | 3231       | 3393       | 3578          |
| Radius (pm)                       |            |            |            |            |            |            |            |            |               |
| M                                 | 162        | 147        | 134        | 130        | 135        | 126        | 125        | 124        | 128           |
| $M^{2+}$                          | —          | 90         | 88         | 85         | 80         | 77         | 75         | 69         | 72            |
| $M^{3+}$                          | 81         | 77         | 74         | 64         | 66         | 60         | 64         | —          | —             |
| Standard reduction potential (V)* | -2.08      | -1.63      | -1.2       | -0.74      | -1.18      | -0.44      | -0.28      | -0.25      | 0.34          |

\*The half-reaction is  $M^{2+}(aq) + 2e^- \longrightarrow M(s)$  (except for Sc and Cr, where the ions are  $Sc^{3+}$  and  $Cr^{3+}$ , respectively).

## Oxidation States

As noted in Chapter 4, the transition metals exhibit variable oxidation states in their compounds. Figure 20.3 shows the oxidation states from scandium to copper. Note that the common oxidation states for each element include +2, +3, or both. The +3 oxidation states are more stable at the beginning of the series, whereas toward the end, the +2 oxidation states are more stable. The reason is

| Sc | Ti | V  | Cr | Mn | Fe | Co | Ni | Cu |
|----|----|----|----|----|----|----|----|----|
|    |    |    |    | +7 |    |    |    |    |
|    |    |    | +6 | +6 | +6 |    |    |    |
|    |    | +5 | +5 | +5 | +5 |    |    |    |
|    | +4 | +4 | +4 | +4 | +4 | +4 |    |    |
| +3 | +3 | +3 | +3 | +3 | +3 | +3 | +3 |    |
| +2 | +2 | +2 | +2 | +2 | +2 | +2 | +2 | +2 |
|    |    |    |    |    |    |    |    | +1 |

**Figure 20.3**

Oxidation states of the first-row transition metals. The most stable oxidation numbers are shown in color. The zero oxidation state is encountered in some compounds, such as  $Ni(CO)_4$  and  $Fe(CO)_5$ .

that the ionization energies increase gradually from left to right. However, the third ionization energy (when an electron is removed from the  $3d$  orbital) increases more sharply than the first and second ionization energies. Because it takes more energy to remove the third electron from the metals near the end of the row than from those near the beginning, the metals near the end tend to form  $M^{2+}$  ions rather than  $M^{3+}$  ions.

**Recall that oxides in which the metal has a high oxidation number are covalent and acidic, whereas those in which the metal has a low oxidation number are ionic and basic (see Section 15.11).**

The highest oxidation state is +7, for manganese ( $4s^23d^5$ ). Transition metals usually exhibit their highest oxidation states in compounds with very electronegative elements such as oxygen and fluorine—for example,  $VF_5$ ,  $CrO_3$ , and  $Mn_2O_7$ .

## 20.2 Coordination Compounds

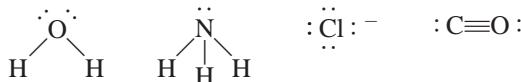
**A complex ion contains a central metal ion bonded to one or more ions or molecules (see Section 17.10). A complex ion can be either a cation or an anion.**

Transition metals have a distinct tendency to form complex ions (see p. 597). A **coordination compound** typically consists of a complex ion and counter ion. [Note that some coordination compounds such as  $Fe(CO)_5$  do not contain complex ions.] Our understanding of the nature of coordination compounds stems from the classic work of the Swiss chemist Alfred Werner, who prepared and characterized many coordination compounds. In 1893, at the age of 26, Werner proposed what is now commonly referred to as *Werner's coordination theory*.

Nineteenth-century chemists were puzzled by a certain class of reactions that seemed to violate valence theory. For example, the valences of the elements in cobalt(III) chloride and in ammonia seem to be completely satisfied, and yet these two substances react to form a stable compound having the formula  $CoCl_3 \cdot 6NH_3$ . To explain this behavior, Werner postulated that most elements exhibit two types of valence: *primary valence* and *secondary valence*. In modern terminology, primary valence corresponds to the oxidation number and secondary valence to the coordination number of the element. In  $CoCl_3 \cdot 6NH_3$ , according to Werner, cobalt has a primary valence of 3 and a secondary valence of 6.

Today we use the formula  $[Co(NH_3)_6]Cl_3$  to indicate that the ammonia molecules and the cobalt atom form a complex ion; the chloride ions are not part of the complex but are held to it by ionic forces. Most, but not all, of the metals in coordination compounds are transition metals.

The molecules or ions that surround the metal in a complex ion are called **ligands** (Table 20.2). The interactions between a metal atom and the ligands can be thought of as Lewis acid-base reactions. As we saw in Section 16.11, a Lewis base is a substance capable of donating one or more electron pairs. Every ligand has at least one unshared pair of valence electrons, as these examples show:



Therefore, ligands play the role of Lewis bases. On the other hand, a transition metal atom (in either its neutral or positively charged state) acts as a Lewis acid, accepting (and sharing) pairs of electrons from the Lewis bases. Thus, the metal-ligand bonds are usually coordinate covalent bonds (see Section 9.9).

The atom in a ligand that is bound directly to the metal atom is known as the **donor atom**. For example, nitrogen is the donor atom in the  $[Cu(NH_3)_4]^{2+}$  complex ion. The **coordination number** in coordination compounds is defined as the number of donor atoms surrounding the central metal atom in a complex ion. For example, the coordination number of  $Ag^+$  in  $[Ag(NH_3)_2]^+$  is 2, that of  $Cu^{2+}$  in

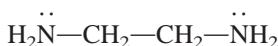
**In a crystal lattice the coordination number of an atom (or ion) is defined as the number of atoms (or ions) surrounding the atom (or ion).**

**TABLE 20.2** Some Common Ligands

| Name                                   | Structure  |
|--|--|
|  | <i>Monodentate ligands</i>   |
| Ammonia                                | $\begin{array}{c} \text{H} \\   \\ \text{H}-\text{N}-\text{H} \\   \\ \text{H} \end{array}$  |
| Carbon monoxide                        | $:\text{C}\equiv\text{O}:^{\cdot\cdot}$  |
| Chloride ion                           | $:\ddot{\text{Cl}}:^-$   |
| Cyanide ion                            | $[\text{:C}\equiv\text{N}:]^-$   |
| Thiocyanate ion                        | $[\text{:S}-\text{C}\equiv\text{N}:]^-$  |
| Water                                  | $\begin{array}{c} \text{H} & \text{O} & \text{H} \\ & \backslash & / \\ & \text{H} & \end{array}$  |
|  | <i>Bidentate ligands</i>   |
| Ethylenediamine                        | $\text{H}_2\ddot{\text{N}}-\text{CH}_2-\text{CH}_2-\ddot{\text{N}}\text{H}_2$  |
| Oxalate ion                            | $\left[ \begin{array}{c} \text{O} & \text{O} \\    &    \\ \text{C} & -\text{C} \\    &    \\ \text{O} & \text{O} \end{array} \right]^{2-}$  |
|  | <i>Polydentate ligand</i>  |
| Ethylenediaminetetraacetate ion (EDTA) | $\left[ \begin{array}{c} \text{O} & & & \text{O} \\    & & &    \\ \text{C} & & & \text{C} \\    & & &    \\ \text{O} & & & \text{O} \\   & & &   \\ \text{O} & & & \text{O} \\   & & &   \\ \text{C} & & & \text{C} \\    & & &    \\ \text{O} & & & \text{O} \\   & & &   \\ \text{O} & & & \text{O} \end{array} \right]^{4-}$ |

$[\text{Cu}(\text{NH}_3)_4]^{2+}$  is 4, and that of  $\text{Fe}^{3+}$  in  $[\text{Fe}(\text{CN})_6]^{3-}$  is 6. The most common coordination numbers are 4 and 6, but coordination numbers such as 2 and 5 are also known.

Depending on the number of donor atoms present, ligands are classified as *monodentate*, *bidentate*, or *polydentate* (see Table 20.2).  $\text{H}_2\text{O}$  and  $\text{NH}_3$  are monodentate ligands with only one donor atom each. One bidentate ligand is ethylenediamine (sometimes abbreviated “en”):

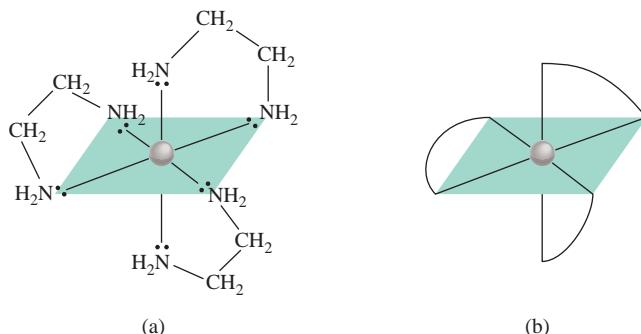


The two nitrogen atoms can coordinate with a metal atom, as shown in Figure 20.4.

*Bidentate and polydentate ligands* are also called **chelating agents** because of their ability to hold the metal atom like a claw (from the Greek *chele*, meaning “claw”). One example is ethylenediaminetetraacetate ion (EDTA), a polydentate ligand used to treat metal poisoning (Figure 20.5). Six donor atoms enable EDTA to form a very stable complex ion with lead, which is removed from the blood and excreted from the body. EDTA is also used to clean up spills of radioactive metals.

**Figure 20.4**

(a) Structure of a metal-ethylenediamine complex cation such as  $[Co(en)_3]^{2+}$ . Each ethylenediamine molecule provides two N donor atoms and is therefore a bidentate ligand.  
 (b) Simplified structure of the same complex cation.



## Oxidation Number of Metals in Coordination Compounds

The net charge of a complex ion is the sum of the charges on the central metal atom and its surrounding ligands. In the  $[PtCl_6]^{2-}$  ion, for example, each chloride ion has an oxidation number of  $-1$ , so the oxidation number of Pt must be  $+4$ . If the ligands do not bear net charges, the oxidation number of the metal is equal to the charge of the complex ion. Thus, in  $[Cu(NH_3)_4]^{2+}$  each  $NH_3$  is neutral, so the oxidation number of Cu is  $+2$ .

### Example 20.1

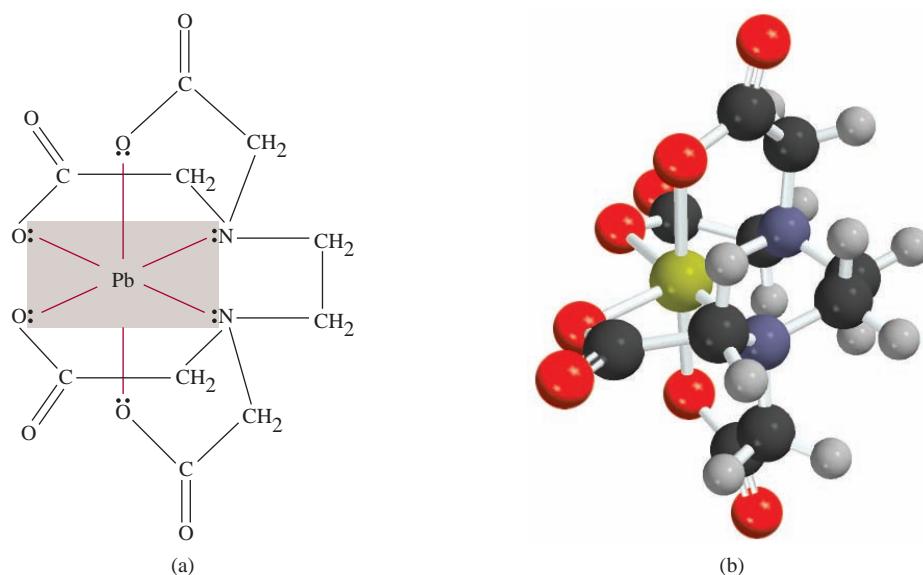
Specify the oxidation number of the central metal atom in each of the following compounds: (a)  $[Ru(NH_3)_5(H_2O)]Cl_2$ , (b)  $[Cr(NH_3)_6](NO_3)_3$ , (c)  $[Fe(CO)_5]$ , and (d)  $K_4[Fe(CN)_6]$ .

**Strategy** The oxidation number of the metal atom is equal to its charge. First we examine the anion or the cation that electrically balances the complex ion. This step gives us the net charge of the complex ion. Next, from the nature of the ligands (charged or neutral species) we can deduce the net charge of the metal and hence its oxidation number.

(Continued)

**Figure 20.5**

(a) EDTA complex of lead. The complex bears a net charge of  $-2$  because each O donor atom has one negative charge and the lead ion carries two positive charges. Only the lone pairs that participate in bonding are shown. (b) Molecular model of the  $Pb^{2+}$ -EDTA complex. The yellow sphere is the  $Pb^{2+}$  ion. Note the octahedral geometry around the  $Pb^{2+}$  ion.



- Solution**
- Both  $\text{NH}_3$  and  $\text{H}_2\text{O}$  are neutral species. Because each chloride ion carries a  $-1$  charge, and there are two  $\text{Cl}^-$  ions, the oxidation number of Ru must be  $+2$ .
  - Each nitrate ion has a charge of  $-1$ ; therefore, the cation must be  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ .  $\text{NH}_3$  is neutral, so the oxidation number of Cr is  $+3$ .
  - Because the CO species are neutral, the oxidation number of Fe is zero.
  - Each potassium ion has a charge of  $+1$ ; therefore, the anion is  $[\text{Fe}(\text{CN})_6]^{4-}$ . Next, we know that each cyanide group bears a charge of  $-1$ , so Fe must have an oxidation number of  $+2$ .

**Practice Exercise** Write the oxidation numbers of the metals in the compound  $\text{K}[\text{Au}(\text{OH})_4]$ .

Similar problems: 20.13, 20.14.

## Naming Coordination Compounds

Now that we have discussed the various types of ligands and the oxidation numbers of metals, our next step is to learn what to call these coordination compounds. The rules for naming coordination compounds are as follows:

- The cation is named before the anion, as in other ionic compounds. The rule holds regardless of whether the complex ion bears a net positive or a negative charge. For example, in the  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  compound, we name the  $\text{K}^+$  and  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  cations first, respectively.
- Within a complex ion the ligands are named first, in alphabetical order, and the metal ion is named last.
- The names of anionic ligands end with the letter *o*, whereas a neutral ligand is usually called by the name of the molecule. The exceptions are  $\text{H}_2\text{O}$  (aqua), CO (carbonyl), and  $\text{NH}_3$  (ammine). Table 20.3 lists some common ligands.

**TABLE 20.3** Names of Common Ligands in Coordination Compounds

| Ligand                               | Name of Ligand in Coordination Compound |
|--------------------------------------|---|
| Bromide, $\text{Br}^-$               | Bromo                                   |
| Chloride, $\text{Cl}^-$              | Chloro                                  |
| Cyanide, $\text{CN}^-$               | Cyano                                   |
| Hydroxide, $\text{OH}^-$             | Hydroxo                                 |
| Oxide, $\text{O}^{2-}$               | Oxo                                     |
| Carbonate, $\text{CO}_3^{2-}$        | Carbonato                               |
| Nitrite, $\text{NO}_2^-$             | Nitro                                   |
| Oxalate, $\text{C}_2\text{O}_4^{2-}$ | Oxalato                                 |
| Ammonia, $\text{NH}_3$               | Ammine                                  |
| Carbon monoxide, CO                  | Carbonyl                                |
| Water, $\text{H}_2\text{O}$          | Aqua                                    |
| Ethylenediamine                      | Ethylenediamine                         |
| Ethylenediaminetetraacetate          | Ethylenediaminetetraacetato             |

**TABLE 20.4****Names of Anions Containing Metal Atoms**

| Metal      | Name of Metal in Anionic Complex |
|------------|----------------------------------|
| Aluminum   | Aluminate                        |
| Chromium   | Chromate                         |
| Cobalt     | Cobaltate                        |
| Copper     | Cuprate                          |
| Gold       | Aurate                           |
| Iron       | Ferrate                          |
| Lead       | Plumbate                         |
| Manganese  | Manganate                        |
| Molybdenum | Molybdate                        |
| Nickel     | Nickelate                        |
| Silver     | Argentate                        |
| Tin        | Stannate                         |
| Tungsten   | Tungstate                        |
| Zinc       | Zincate                          |

- When several ligands of a particular kind are present, we use the Greek prefixes *di-*, *tri-*, *tetra-*, *penta-*, and *hexa-* to name them. Thus, the ligands in the cation  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  are “tetraamminedichloro.” (Note that prefixes are ignored when alphabetizing ligands.) If the ligand itself contains a Greek prefix, we use the prefixes *bis* (2), *tris* (3), and *tetrakis* (4) to indicate the number of ligands present. For example, the ligand ethylenediamine already contains *di*; therefore, if two such ligands are present the name is *bis(ethylenediamine)*.
- The oxidation number of the metal is written in Roman numerals following the name of the metal. For example, the Roman numeral III is used to indicate the +3 oxidation state of chromium in  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ , which is called tetraamminedichlorochromium(III) ion.
- If the complex is an anion, its name ends in *-ate*. For example, in  $\text{K}_4[\text{Fe}(\text{CN})_6]$  the anion  $[\text{Fe}(\text{CN})_6]^{4-}$  is called hexacyanoferrate(II) ion. Note that the Roman numeral II indicates the oxidation state of iron. Table 20.4 gives the names of anions containing metal atoms.

**Example 20.2**

Write the systematic names of the following coordination compounds: (a)  $\text{Ni}(\text{CO})_4$ , (b)  $\text{NaAuF}_4$ , (c)  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , (d)  $[\text{Cr}(\text{en})_3]\text{Cl}_3$ .

**Strategy** We follow the preceding procedure for naming coordination compounds and refer to Tables 20.3 and 20.4 for names of ligands and anions containing metal atoms.

- Solution** (a) The CO ligands are neutral species and therefore the Ni atom bears no net charge. The compound is called tetracarbonylnickel(0), or more commonly, nickel tetracarbonyl.
- (b) The sodium cation has a positive charge; therefore, the complex anion has a negative charge ( $\text{AuF}_4^-$ ). Each fluoride ion has a negative charge so the oxidation number of gold must be +3 (to give a net negative charge). The compound is called sodium tetrafluoroaurate(III).
- (c) The complex ion is the anion and it bears three negative charges because each potassium ion bears a +1 charge. Looking at  $[\text{Fe}(\text{CN})_6]^{3-}$ , we see that the oxidation number of Fe must be +3 because each cyanide ion bears a -1 charge (-6 total). The compound is potassium hexacyanoferrate(III). This compound is commonly called potassium ferricyanide.
- (d) As we noted earlier, *en* is the abbreviation for the ligand ethylenediamine. Because there are three chloride ions each with a -1 charge, the cation is  $[\text{Cr}(\text{en})_3]^{3+}$ . The *en* ligands are neutral so the oxidation number of Cr must be +3. Because there are three *en* groups present and the name of the ligand already contains *di* (rule 4), the compound is called *tris(ethylenediamine)chromium(III) chloride*.

**Practice Exercise** What is the systematic name of  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ ?

**Example 20.3**

Write the formulas for the following compounds: (a) pentaamminechlorocobalt(III) chloride, (b) dichlorobis(ethylenediamine)platinum(IV) nitrate, (c) sodium hexanitrocobaltate(III).

**Strategy** We follow the preceding procedure and refer to Tables 20.3 and 20.4 for names of ligands and anions containing metal atoms.

(Continued)

**Solution** (a) The complex cation contains five  $\text{NH}_3$  groups, a  $\text{Cl}^-$  ion, and a Co ion having a +3 oxidation number. The net charge of the cation must be +2,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ . Two chloride anions are needed to balance the positive charges. Therefore, the formula of the compound is  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ .

- (b) There are two chloride ions (−1 each), two *en* groups (neutral), and a Pt ion with an oxidation number of +4. The net charge on the cation must be +2,  $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$ . Two nitrate ions are needed to balance the +2 charge of the complex cation. Therefore, the formula of the compound is  $[\text{Pt}(\text{en})_2\text{Cl}_2](\text{NO}_3)_2$ .
- (c) The complex anion contains six nitro groups (−1 each) and a cobalt ion with an oxidation number of +3. The net charge on the complex anion must be −3,  $[\text{Co}(\text{NO}_2)_6]^{3-}$ . Three sodium cations are needed to balance the −3 charge of the complex anion. Therefore, the formula of the compound is  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ .

Similar problems: 20.17, 20.18.

**Practice Exercise** Write the formula for the following compound: *tris(ethylene-diamine)cobalt(III)* sulfate.

## 20.3 Geometry of Coordination Compounds

Figure 20.6 shows four different geometric arrangements for metal atoms with monodentate ligands. In these diagrams we see that the structure and the coordination number of the metal atom relate to each other as follows:

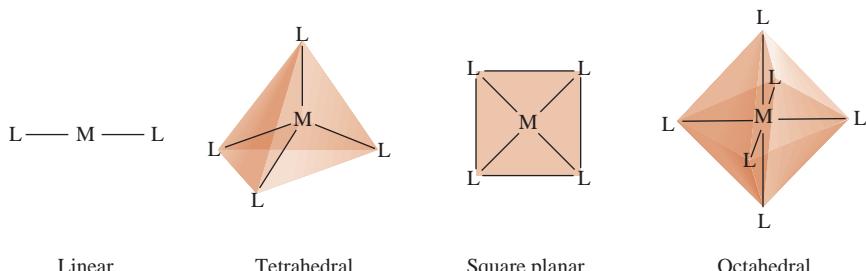
| Coordination Number | Structure                    |
|---------------------|------------------------------|
| 2                   | Linear                       |
| 4                   | Tetrahedral or square planar |
| 6                   | Octahedral                   |

### Coordination Number = 2

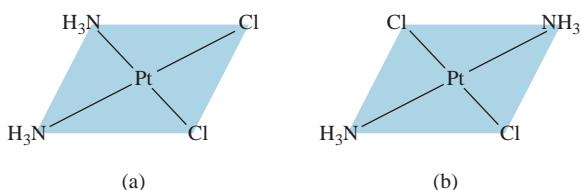
The  $[\text{Ag}(\text{NH}_3)_2]^+$  complex ion, formed by the reaction between  $\text{Ag}^+$  ions and ammonia (see Table 17.4), has a coordination number of 2 and a linear geometry. Other examples are  $[\text{CuCl}_2]^-$  and  $[\text{Au}(\text{CN})_2]^-$ .

### Coordination Number = 4

There are two types of geometries with a coordination number of 4. The  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  and  $[\text{CoCl}_4]^{2-}$  ions have tetrahedral geometry, whereas the  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  ion has the square planar geometry. In Chapter 11 we discussed geometric isomers of alkenes (see p. 365). Square planar complex ions with two different monodentate ligands can also



**Figure 20.6**  
Common geometries of complex ions. In each case M is a metal and L is a monodentate ligand.



**Figure 20.7**

The (a) *cis* and (b) *trans* isomers of diamminedichloroplatinum(II),  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ . Note that the two Cl atoms are adjacent to each other in the *cis* isomer and diagonally across from each other in the *trans* isomer.

exhibit geometric isomerism. Figure 20.7 shows the *cis* and *trans* isomers of diamminedichloroplatinum(II). Note that although the types of bonds are the same in both isomers (two Pt—N and two Pt—Cl bonds), the spatial arrangements are different. These two isomers have different properties (melting point, boiling point, color, solubility in water, and dipole moment).

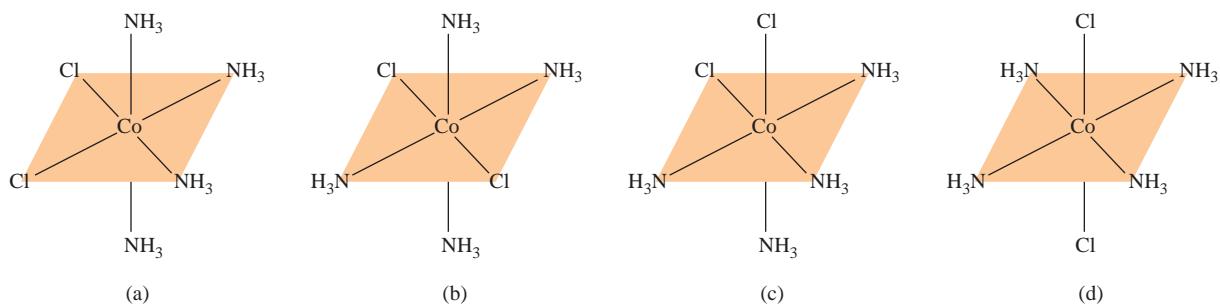


**Figure 20.9**  
Left: *cis*-tetraamminedichloro-cobalt(III) chloride (left). Right: *trans*-tetraamminedichloro-cobalt(III) chloride (right).

### **Coordination Number = 6**

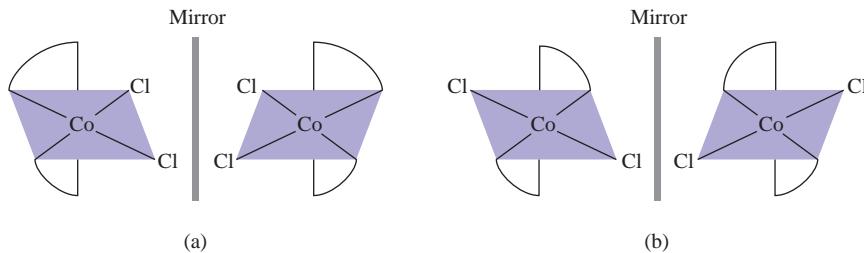
Complex ions with a coordination number of 6 all have octahedral geometry (see Section 10.1). Geometric isomers are possible in octahedral complexes when two or more different ligands are present. An example is the tetraamminedichlorocobalt(III) ion shown in Figure 20.8. The two geometric isomers have different colors and other properties even though they have the same ligands and the same number and types of bonds (Figure 20.9).

In addition to geometric isomers, certain octahedral complex ions can also give rise to enantiomers, as discussed in Chapter 11. Figure 20.10 shows the *cis* and *trans* isomers of dichlorobis(ethylenediamine)cobalt(III) ion and their mirror images. Careful examination reveals that the *trans* isomer and its mirror image are superimposable, but the *cis* isomer and its mirror image are not. Therefore, the *cis* isomer and its mirror image are enantiomers. It is interesting to note that unlike the case in most organic compounds, there are no asymmetric carbon atoms in these compounds.



**Figure 20.8**

The (a) *cis* and (b) *trans* isomers of tetraamminedichlorocobalt(III) ion,  $[Co(NH_3)_4Cl_2]^+$ . The structure shown in (c) can be generated by rotating that in (a), and the structure shown in (d) can be generated by rotating that in (b). The ion has only two geometric isomers, (a) [or (c)] and (b) [or (d)].

**Figure 20.10**

The (a) *cis* and (b) *trans* isomers of dichlorobis(ethylenediamine)cobalt(III) ion,  $[Co(en)_2Cl_2]^+$ , and their mirror images. If you could rotate the mirror image in (b) 90° clockwise about the vertical position and place the ion over the *trans* isomer, you would find that the two are superimposable. No matter how you rotated the *cis* isomer and its mirror image, however, you could not superimpose one on the other.

## 20.4 Bonding in Coordination Compounds: Crystal Field Theory

A satisfactory theory of bonding in coordination compounds must account for properties such as color and magnetism, as well as stereochemistry and bond strength. No single theory as yet does all this for us. Rather, several different approaches have been applied to transition metal complexes. We will consider only one of them here—crystal field theory—because it accounts for both the color and magnetic properties of many coordination compounds.

We will begin our discussion of crystal field theory with the most straightforward case, namely, complex ions with octahedral geometry. Then we will see how it is applied to tetrahedral and square-planar complexes.

### Crystal Field Splitting in Octahedral Complexes

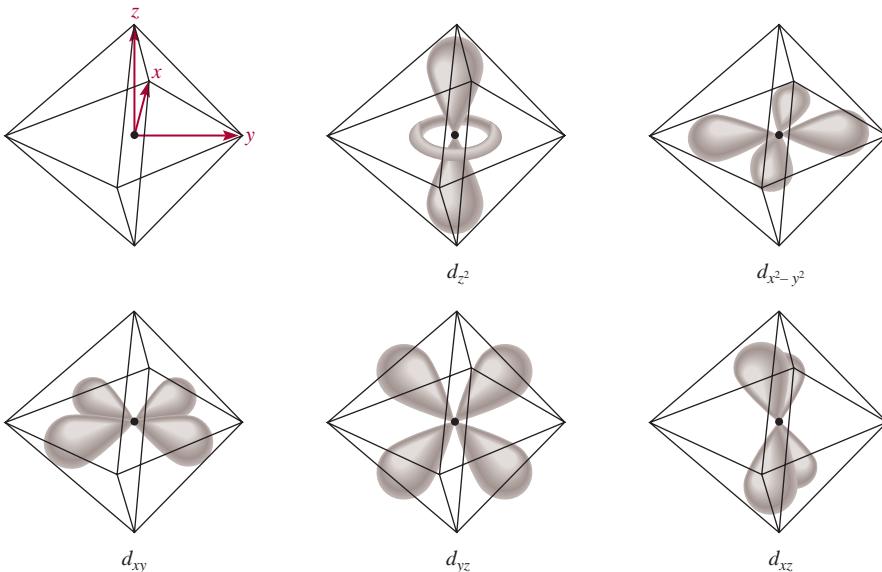
Crystal field theory explains the bonding in complex ions purely in terms of electrostatic forces. In a complex ion, two types of electrostatic interaction come into play. One is the attraction between the positive metal ion and the negatively charged ligand or the negatively charged end of a polar ligand. This is the force that binds the ligands to the metal. The second type of interaction is electrostatic repulsion between the lone pairs on the ligands and the electrons in the *d* orbitals of the metals.

The name “crystal field” is associated with the theory used to explain the properties of solid, crystalline materials. The same theory is used to study coordination compounds.

As we saw in Chapter 7, *d* orbitals have different orientations, but in the absence of external disturbance they all have the same energy. In an octahedral complex, a central metal atom is surrounded by six lone pairs of electrons (on the six ligands), so all five *d* orbitals experience electrostatic repulsion. The magnitude of this repulsion depends on the orientation of the *d* orbital that is involved. Take the  $d_{x^2-y^2}$  orbital as an example. In Figure 20.11, we see that the lobes of this orbital point toward corners of the octahedron along the *x* and *y* axes, where the lone-pair electrons are positioned. Thus, an electron residing in this orbital would experience a greater repulsion from the ligands than an electron would in, say, the  $d_{xy}$  orbital. For this reason, the energy of the  $d_{x^2-y^2}$  orbital is increased relative to the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  orbitals. The  $d_{z^2}$  orbital’s energy is also greater, because its lobes are pointed at the ligands along the *z* axis.

**Figure 20.11**

The five  $d$  orbitals in an octahedral environment. The metal atom (or ion) is at the center of the octahedron, and the six lone pairs on the donor atoms of the ligands are at the corners.



As a result of these metal-ligand interactions, the five  $d$  orbitals in an octahedral complex are split between two sets of energy levels: a higher level with two orbitals ( $d_{x^2-y^2}$  and  $d_z^2$ ) having the same energy and a lower level with three equal-energy orbitals ( $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$ ), as shown in Figure 20.12. The **crystal field splitting** ( $\Delta$ ) is the energy difference between two sets of  $d$  orbitals in a metal atom when ligands are present. The magnitude of  $\Delta$  depends on the metal and the nature of the ligands: it has a direct effect on the color and magnetic properties of complex ions.

## Color

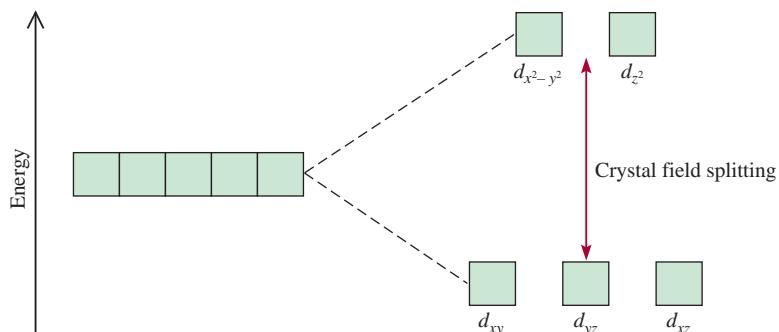


In Chapter 7 we learned that white light, such as sunlight, is a combination of all colors. A substance appears black if it absorbs all the visible light that strikes it. If it absorbs no visible light, it is white or colorless. An object appears green if it absorbs all light but reflects the green component. An object also looks green if it reflects all colors except red, the *complementary* color of green (Figure 20.13).

What has been said of reflected light also applies to transmitted light (that is, the light that passes through the medium, for example, a solution). Consider the hydrated cupric ion,  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ , which absorbs light in the orange region of the spectrum so that a solution of  $\text{CuSO}_4$  appears blue to us. Recall from Chapter 7 that when the

**Figure 20.12**

Crystal field splitting between  $d$  orbitals in an octahedral complex.



energy of a photon is equal to the difference between the ground state and an excited state, absorption occurs as the photon strikes the atom (or ion or compound), and an electron is promoted to a higher level. This knowledge enables us to calculate the energy change involved in the electron transition. The energy of a photon, given by Equation (7.2), is

$$E = h\nu$$

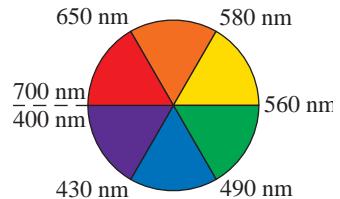
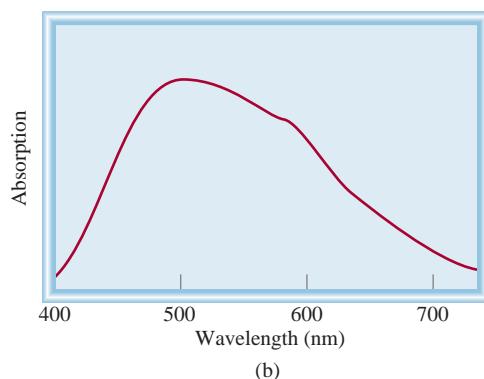
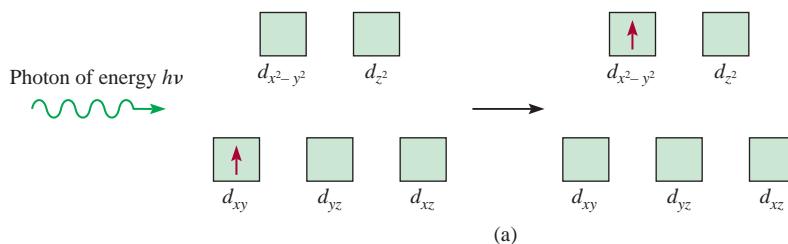
where  $h$  represents Planck's constant ( $6.63 \times 10^{-34} \text{ J} \cdot \text{s}$ ) and  $\nu$  is the frequency of the radiation, which is  $5.00 \times 10^{14}/\text{s}$  for a wavelength of 600 nm. Here  $E = \Delta$ , so we have

$$\begin{aligned}\Delta &= h\nu \\ &= (6.63 \times 10^{-34} \text{ J} \cdot \text{s})(5.00 \times 10^{14}/\text{s}) \\ &= 3.32 \times 10^{-19} \text{ J}\end{aligned}$$

(Note that this is the energy absorbed by one ion.) If the wavelength of the photon absorbed by an ion lies outside the visible region, then the transmitted light looks the same (to us) as the incident light—white—and the ion appears colorless.

The best way to measure crystal field splitting is to use spectroscopy to determine the wavelength at which light is absorbed. The  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion provides a straightforward example, because  $\text{Ti}^{3+}$  has only one  $3d$  electron (Figure 20.14). The  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion absorbs light in the visible region of the spectrum (Figure 20.15). The wavelength corresponding to maximum absorption is 498 nm [Figure 20.14(b)]. This information enables us to calculate the crystal field splitting as follows. We start by writing

$$\Delta = h\nu \quad (20.1)$$



**Figure 20.13**  
A color wheel with appropriate wavelengths. Complementary colors, such as red and green, are on opposite sides of the wheel.

**Figure 20.14**  
(a) The process of photon absorption and (b) a graph of the absorption spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ . The energy of the incoming photon is equal to the crystal field splitting. The maximum absorption peak in the visible region occurs at 498 nm.

**Figure 20.15**

*Colors of some of the first-row transition metal ions in solution. From left to right:  $Ti^{3+}$ ,  $Cr^{3+}$ ,  $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ . The  $Sc^{3+}$  and  $V^{5+}$  ions are colorless.*



Also

Equation (7.1) shows that  $c = \lambda\nu$ .

$$\nu = \frac{c}{\lambda}$$

where  $c$  is the speed of light and  $\lambda$  is the wavelength. Therefore,

$$\begin{aligned}\Delta &= \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(498 \text{ nm})(1 \times 10^{-9} \text{ m}/1 \text{ nm})} \\ &= 3.99 \times 10^{-19} \text{ J}\end{aligned}$$

This is the energy required to excite *one*  $[Ti(H_2O)_6]^{3+}$  ion. To express this energy difference in the more convenient units of kilojoules per mole, we write

$$\begin{aligned}\Delta &= (3.99 \times 10^{-19} \text{ J/ion})(6.02 \times 10^{23} \text{ ions/mol}) \\ &= 240,000 \text{ J/mol} \\ &= 240 \text{ kJ/mol}\end{aligned}$$

Aided by spectroscopic data for a number of complexes, all having the same metal ion but different ligands, chemists calculated the crystal splitting for each ligand and established a *spectrochemical series*, which is a *list of ligands arranged in increasing order of their abilities to split the d orbital energy levels*:

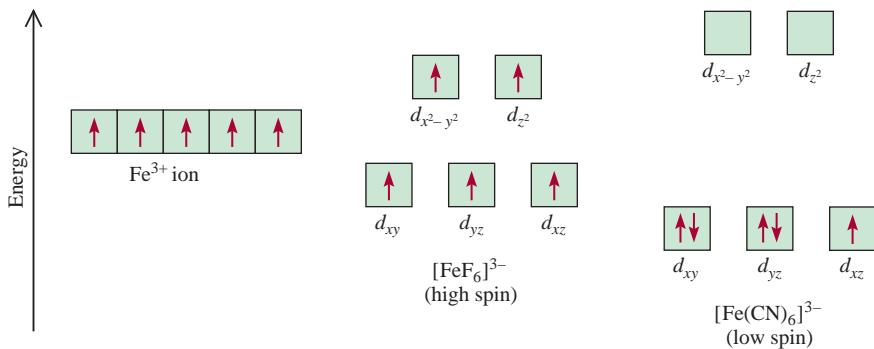


These ligands are arranged in the order of increasing value of  $\Delta$ . CO and  $CN^-$  are called *strong-field ligands*, because they cause a large splitting of the  $d$  orbital energy levels. The halide ions and hydroxide ion are *weak-field ligands*, because they split the  $d$  orbitals to a lesser extent.

## Magnetic Properties

The magnitude of the crystal field splitting also determines the magnetic properties of a complex ion. The  $[Ti(H_2O)_6]^{3+}$  ion, having only one  $d$  electron, is always paramagnetic. However, for an ion with several  $d$  electrons, the situation is less clearcut. Consider, for example, the octahedral complexes  $[FeF_6]^{3-}$  and  $[Fe(CN)_6]^{3-}$  (Figure 20.16). The electron configuration of  $Fe^{3+}$  is  $[Ar]3d^5$ , and there are two possible ways to distribute the five  $d$  electrons among the  $d$  orbitals. According to Hund's rule (see Section 7.8), maximum stability is reached when the electrons are placed in five separate orbitals with parallel spins. But this arrangement can be achieved only at a cost; two of the five electrons must be promoted to the higher-energy  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals.

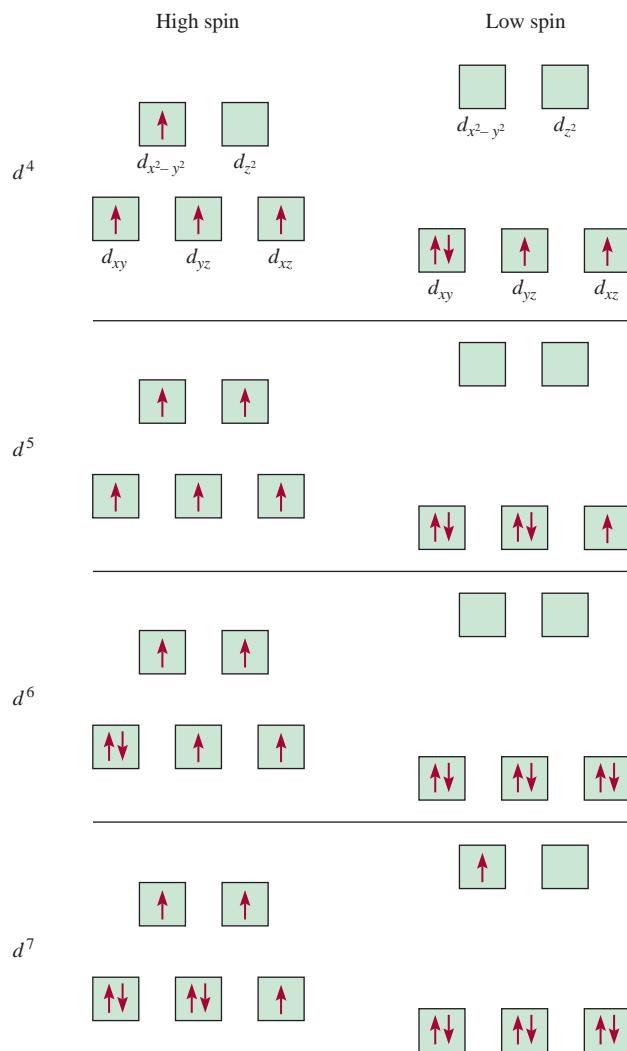
The order in the spectrochemical series is the same no matter which metal atom (or ion) is present.



**Figure 20.16**  
Energy-level diagrams for the  $\text{Fe}^{3+}$  ion and for the  $[\text{FeF}_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  complex ions.

No such energy investment is needed if all five electrons enter the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals. According to Pauli's exclusion principle (p. 228), there will be only one unpaired electron present in this case.

Figure 20.17 shows the distribution of electrons among  $d$  orbitals that results in low- and high-spin complexes. The actual arrangement of the electrons is determined by the amount of stability gained by having maximum parallel spins versus the



**Figure 20.17**  
Orbital diagrams for the high-spin and low-spin octahedral complexes corresponding to the electron configurations  $d^4$ ,  $d^5$ ,  $d^6$ , and  $d^7$ . No such distinctions can be made for  $d^1$ ,  $d^2$ ,  $d^3$ ,  $d^8$ ,  $d^9$ , and  $d^{10}$ .

investment in energy required to promote electrons to higher  $d$  orbitals. Because  $\text{F}^-$  is a weak-field ligand, the five  $d$  electrons enter five separate  $d$  orbitals with parallel spins to create a high-spin complex (see Figure 20.16). On the other hand, the cyanide ion is a strong-field ligand, so it is energetically preferable for all five electrons to be in the lower orbitals and therefore a low-spin complex is formed. High-spin complexes are more paramagnetic than low-spin complexes.

The magnetic properties of a complex ion depend on the number of unpaired electrons present.

The actual number of unpaired electrons (or spins) in a complex ion can be found by magnetic measurements, and in general, experimental findings support predictions based on crystal field splitting. However, a distinction between low- and high-spin complexes can be made only if the metal ion contains more than three and fewer than eight  $d$  electrons, as shown in Figure 20.17.

### Example 20.4

Predict the number of unpaired spins in the  $[\text{Cr}(\text{en})_3]^{2+}$  ion.

**Strategy** The magnetic properties of a complex ion depend on the strength of the ligands. Strong-field ligands, which cause a high degree of splitting among the  $d$  orbital energy levels, result in low-spin complexes. Weak-field ligands, which cause a small degree of splitting among the  $d$  orbital energy levels, result in high-spin complexes.

**Solution** The electron configuration of  $\text{Cr}^{2+}$  is  $[\text{Ar}]3d^4$ . Because en is a strong-field ligand, we expect  $[\text{Cr}(\text{en})_3]^{2+}$  to be a low-spin complex. According to Figure 20.17, all four electrons will be placed in the lower-energy  $d$  orbitals ( $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$ ) and there will be a total of two unpaired spins.

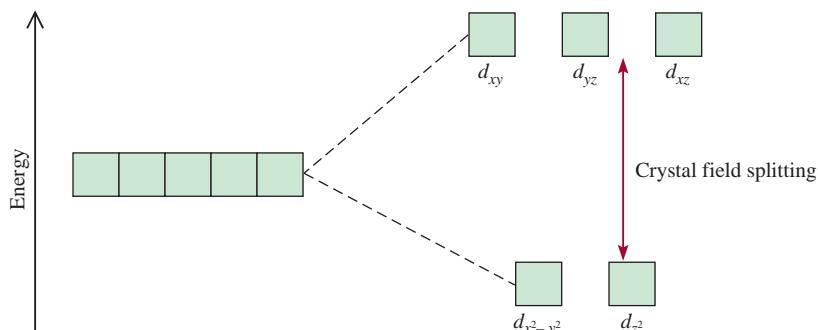
Similar problem: 20.30.

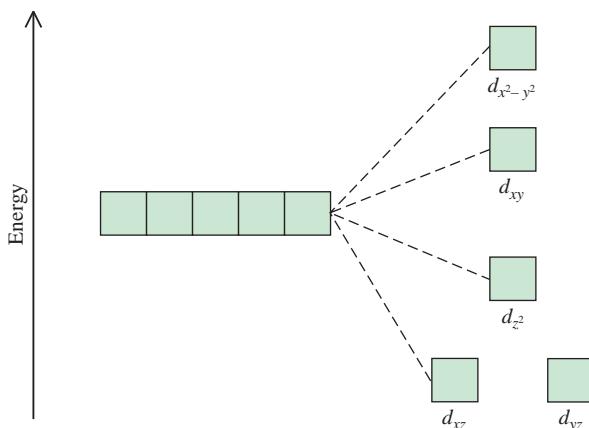
**Practice Exercise** How many unpaired spins are in  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ? ( $\text{H}_2\text{O}$  is a weak-field ligand.)

### Tetrahedral and Square-Planar Complexes

So far we have concentrated on octahedral complexes. The splitting of the  $d$  orbital energy levels in two other types of complexes—tetrahedral and square-planar—can also be accounted for satisfactorily by the crystal field theory. In fact, the splitting pattern for a tetrahedral ion is just the reverse of that for octahedral complexes. In this case, the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals are more closely directed at the ligands and therefore have more energy than the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals (Figure 20.18). Most tetrahedral complexes are high-spin complexes. Presumably, the tetrahedral arrangement reduces the magnitude of metal-ligand interactions, resulting in a smaller  $\Delta$  value. This is a reasonable assumption because the number of ligands is smaller in a tetrahedral complex.

**Figure 20.18**  
Crystal field splitting between  $d$  orbitals in a tetrahedral complex.





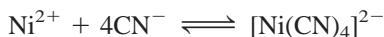
**Figure 20.19**  
Energy-level diagram for a square-planar complex. Because there are more than two energy levels, we cannot define crystal field splitting as we can for octahedral and tetrahedral complexes.

As Figure 20.19 shows, the splitting pattern for square-planar complexes is the most complicated. Clearly, the  $d_{x^2-y^2}$  orbital possesses the highest energy (as in the octahedral case), and the  $d_{xy}$  orbital the next highest. However, the relative placement of the  $d_{z^2}$  and the  $d_{xz}$  and  $d_{yz}$  orbitals cannot be determined simply by inspection and must be calculated.

## 20.5 Reactions of Coordination Compounds

Complex ions undergo ligand exchange (or substitution) reactions in solution. The rates of these reactions vary widely, depending on the nature of the metal ion and the ligands.

In studying ligand exchange reactions, it is often useful to distinguish between the stability of a complex ion and its tendency to react, which we call *kinetic lability*. Stability in this context is a thermodynamic property, which is measured in terms of the species' formation constant  $K_f$  (see p. 598). For example, we say that the complex ion tetracyanonickelate(II) is stable because it has a large formation constant ( $K_f \approx 1 \times 10^{30}$ )



By using cyanide ions labeled with the radioactive isotope carbon-14, chemists have shown that  $[\text{Ni}(\text{CN})_4]^{2-}$  undergoes ligand exchange very rapidly in solution. The following equilibrium is established almost as soon as the species are mixed:



where the asterisk denotes a  $^{14}\text{C}$  atom. Complexes like the tetracyanonickelate(II) ion are termed **labile complexes** because they *undergo rapid ligand exchange reactions*. Thus, a thermodynamically stable species (that is, one that has a large formation constant) is not necessarily unreactive. (In Section 14.4 we saw that the smaller the activation energy, the larger the rate constant, and hence the greater the rate.)

A complex that is thermodynamically *unstable* in acidic solution is  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . The equilibrium constant for the following reaction is about  $1 \times 10^{20}$ :



When equilibrium is reached, the concentration of the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ion is very low. However, this reaction requires several days to complete because of the inertness of the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ion. This is an example of an **inert complex**, a complex ion that undergoes very slow exchange reactions (on the order of hours or even days). It shows

that a thermodynamically unstable species is not necessarily chemically reactive. The rate of reaction is determined by the energy of activation, which is high in this case.

Most complex ions containing  $\text{Co}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Pt}^{2+}$  are kinetically inert. Because they exchange ligands very slowly, they are easy to study in solution. As a result, our knowledge of the bonding, structure, and isomerism of coordination compounds has come largely from studies of these compounds.

## 20.6 Coordination Compounds in Living Systems

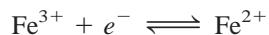
Coordination compounds play many roles in animals and plants. They are essential in the storage and transport of oxygen, as electron transfer agents, as catalysts, and in photosynthesis. Here we will briefly discuss the coordination compounds containing the porphyrin group and cisplatin as an anticancer drug.

### Hemoglobin and Related Compounds

Hemoglobin functions as an oxygen carrier for metabolic processes. The molecule contains four folded long chains called *subunits*. Hemoglobin carries oxygen in the blood from the lungs to the tissues, where it delivers the oxygen molecules to myoglobin. Myoglobin, which is made up of only one subunit, stores oxygen for metabolic processes in muscle.

The *heme* group in each subunit is a complex ion formed between a  $\text{Fe}^{2+}$  ion and a porphyrin group [Figure 20.20(a)]. The  $\text{Fe}^{2+}$  ion is coordinated to the four nitrogen atoms in the porphyrin group and also to a nitrogen donor atom in a ligand that is part of the protein molecule. The sixth ligand is a water molecule, which binds to the ion on the other side of the planar ring to complete the octahedral geometry [Figure 20.20(b)]. In this state, the molecule is called *deoxyhemoglobin* and imparts a bluish tinge to venous blood. The water ligand can be replaced readily by molecular oxygen to form the red *oxyhemoglobin* found in arterial blood.

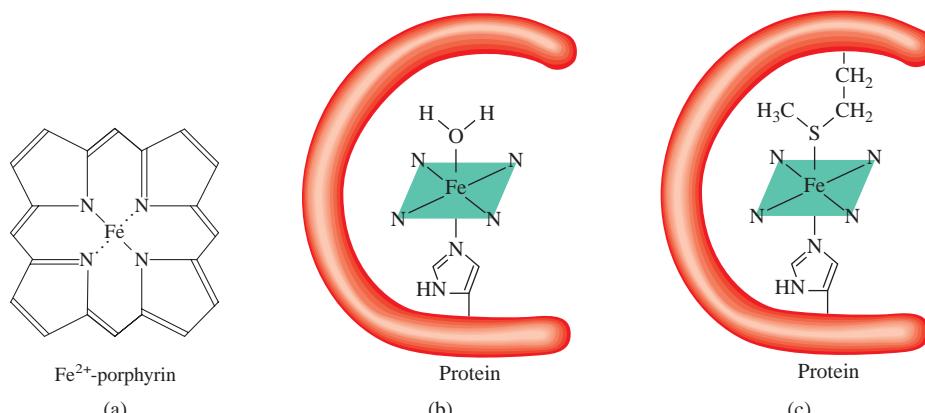
The iron-heme complex is present in another class of proteins called the *cytochromes*. Here too, the iron forms an octahedral complex, but both the fifth and sixth ligands are part of the protein structure [Figure 20.20(c)]. Because the ligands are firmly bound to the metal ion, they cannot be displaced by oxygen or other ligands. Instead, the cytochromes act as electron carriers, which are essential to metabolic processes. In cytochromes, iron undergoes rapid reversible redox processes:

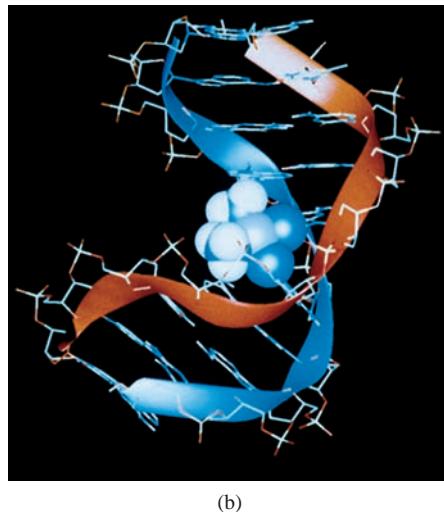
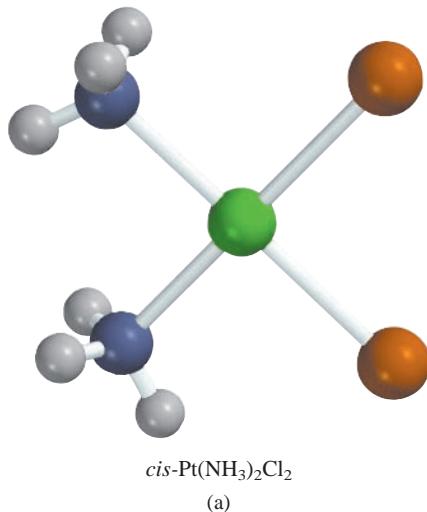


which are coupled to the oxidation of organic molecules such as the carbohydrates.

**Figure 20.20**

(a) Structure of  $\text{Fe}^{2+}$ -porphyrin.  
 (b) The heme group in hemoglobin. The  $\text{Fe}^{2+}$  ion is coordinated with the nitrogen atoms of the heme group. The ligand below the porphyrin is the histidine group, which is part of the protein. The sixth ligand is a water molecule, which can be replaced by oxygen. (c) The heme group in cytochromes. The ligands above and below the porphyrin are the methionine group and histidine group of the protein molecule.



**Figure 20.21**

(a) *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>.  
(b) Cisplatin disrupts DNA replication and transcription by binding to the double helix. The structure of this major DNA adduct, depicted here, was elucidated by Professor Stephen Lippard's group at MIT.

The chlorophyll molecule, which is necessary for plant photosynthesis, also contains the porphyrin ring, but in this case the metal ion is Mg<sup>2+</sup> rather than Fe<sup>2+</sup>.

## Cisplatin

In the mid-1960s, scientists discovered that *cis*-diamminedichloroplatinum(II), *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>], also called cisplatin, is an effective drug for certain types of cancer (see Figure 20.7). The mechanism for the action of cisplatin is the chelation of DNA (deoxyribonucleic acid). Cisplatin binds to DNA by forming cross-links in which the two chloride ions on cisplatin are replaced by nitrogen donor atoms on the DNA molecule (Figure 20.21). This action leads to a mistake (mutation) in the DNA's replication and the eventual destruction of the cancerous cell. Interestingly, the geometric isomer, *trans*-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>], has no anticancer effect because it lacks the ability to bind to DNA.

## KEY EQUATION

$$\Delta = h\nu \quad (20.1) \quad \text{Calculating crystal-field splitting.}$$

## SUMMARY OF FACTS AND CONCEPTS

- Transition metals usually have incompletely filled *d* subshells and a pronounced tendency to form complexes. Compounds that contain complex ions are called coordination compounds.
- The first-row transition metals (scandium to copper) are the most common of all the transition metals; their chemistry is characteristic, in many ways, of the entire group.
- Complex ions consist of a metal ion surrounded by ligands. The donor atoms in the ligands each contribute an electron pair to the central metal ion in a complex.
- Coordination compounds may exist as geometric isomers and/or enantiomers.
- Crystal field theory explains bonding in complexes in terms of electrostatic interactions. According to crystal field theory, the *d* orbitals are split into two higher-energy and three lower-energy orbitals in an octahedral complex. The energy difference between these two sets of *d* orbitals is the crystal field splitting.
- Strong-field ligands cause a large crystal field splitting, and weak-field ligands cause a small splitting. Electron

spins tend to be parallel with weak-field ligands and paired with strong-field ligands, where a greater investment of energy is required to promote electrons into the high-lying *d* orbitals.

- Complex ions undergo ligand exchange reactions in solution.
- Coordination compounds occur in nature and are used as therapeutic drugs.

## KEY WORDS

Chelating agent, p. 689  
 Coordination compound, p. 688  
 Coordination number, p. 688

Crystal field splitting  
 $(\Delta)$ , p. 696  
 Donor atom, p. 688

Inert complex, p. 701  
 Labile complex, p. 701  
 Ligand, p. 688

Spectrochemical series, p. 698

## QUESTIONS AND PROBLEMS

### Properties of Transition Metals

#### Review Questions

- What distinguishes a transition metal from a representative metal?
- Why is zinc not considered a transition metal?
- Explain why atomic radii decrease very gradually from scandium to copper.
- Without referring to the text, write the ground-state electron configurations of the first-row transition metals. Explain any irregularities.
- Write the electron configurations of these ions:  $\text{V}^{5+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Ti}^{4+}$ .
- Why do transition metals have more oxidation states than other elements? Give the highest oxidation states for scandium to copper.
- As we read across the first-row transition metals from left to right, the +2 oxidation state becomes more stable in comparison with the +3 state. Why is this so?
- Chromium exhibits several oxidation states in its compounds, whereas aluminum exhibits only the +3 oxidation state. Explain.

### Coordination Compounds: Nomenclature; Oxidation Number

#### Review Questions

- Define the following terms: coordination compound, ligand, donor atom, coordination number, chelating agent.
- Describe the interaction between a donor atom and a metal atom in terms of a Lewis acid-base reaction.

#### Problems

- Complete these statements for the complex ion  $[\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{CN}]^{2+}$ . (a) The term “en” is the abbreviation for \_\_\_\_\_. (b) The oxidation number of Co is \_\_\_\_\_. (c) The coordination number of Co is \_\_\_\_\_. (d) \_\_\_\_\_ is a bidentate ligand.
- Complete these statements for the complex ion  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]^{2-}$ . (a) The oxidation number of Cr is \_\_\_\_\_. (b) The coordination number of Cr is \_\_\_\_\_. (c) \_\_\_\_\_ is a bidentate ligand.
- Give the oxidation numbers of the metals in these species: (a)  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , (b)  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ , (c)  $[\text{Ni}(\text{CN})_4]^{2-}$ .
- Give the oxidation numbers of the metals in these species: (a)  $\text{Na}_2\text{MoO}_4$ , (b)  $\text{MgWO}_4$ , (c)  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .
- What are the systematic names for these ions and compounds: (a)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ , (b)  $\text{Cr}(\text{NH}_3)_3\text{Cl}_3$ , (c)  $[\text{Co}(\text{en})_2\text{Br}_2]^+$ , (d)  $\text{Fe}(\text{CO})_5$ ?
- What are the systematic names for these ions and compounds: (a)  $[\text{cis}-\text{Co}(\text{en})_2\text{Cl}_2]^+$ , (b)  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$ , (c)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , (d)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ , (e)  $\text{trans}-\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ ?
- Write the formulas for each of these ions and compounds: (a) tetrahydroxozincate(II), (b) penta-aquochlorochromium(III) chloride, (c) tetrabromo-cuprate(II), (d) ethylenediaminetetraacetatoferrate(II).
- Write the formulas for each of these ions and compounds: (a) bis(ethylenediamine) dichlorochromium(III), (b) pentacarbonyliron(0), (c) potassium tetracyanocuprate(II), (d) tetraammineaquochlorocobalt(III) chloride.

## Structure of Coordination Compounds

### Problems

- 20.19** Draw structures of all the geometric and optical isomers of each of these cobalt complexes:
- $[\text{Co}(\text{NH}_3)_6]^{3+}$
  - $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$
  - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
  - $[\text{Co}(\text{en})_3]^{3+}$
  - $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$
- 20.20** How many geometric isomers are in these species: (a)  $[\text{Co}(\text{NH}_3)_2\text{Cl}_4]^-$ , (b)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ ?
- 20.21** A student prepared a cobalt complex that has one of the following structures:  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ , or  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ . Explain how the student would distinguish among these possibilities by an electrical conductance experiment. At the student's disposal are three strong electrolytes:  $\text{NaCl}$ ,  $\text{MgCl}_2$ , and  $\text{FeCl}_3$ , which may be used for comparison purposes.
- 20.22** The complex ion  $[\text{Ni}(\text{CN})_2\text{Br}_2]^{2-}$  has a square planar geometry. Draw the structures of the geometric isomers of this complex.

## Bonding, Color, Magnetism

### Review Questions

- 20.23** Briefly describe the crystal field theory. Define the following terms: crystal field splitting, high-spin complex, low-spin complex, spectrochemical series.
- 20.24** What is the origin of color in a compound?
- 20.25** Compounds containing the  $\text{Sc}^{3+}$  ion are colorless, whereas those containing the  $\text{Ti}^{3+}$  ion are colored. Explain.
- 20.26** What factors determine whether a given complex will be diamagnetic or paramagnetic?

### Problems

- 20.27** For the same type of ligands, explain why the crystal field splitting for an octahedral complex is always greater than that for a tetrahedral complex.
- 20.28** Transition metal complexes containing  $\text{CN}^-$  ligands are often yellow, whereas those containing  $\text{H}_2\text{O}$  ligands are often green or blue. Explain.
- 20.29** The  $[\text{Ni}(\text{CN})_4]^{2-}$  ion, which has a square planar geometry, is diamagnetic, whereas the  $[\text{NiCl}_4]^{2-}$  ion, which has a tetrahedral geometry, is paramagnetic. Show the crystal field splitting diagrams for those two complexes.
- 20.30** Predict the number of unpaired electrons in these complex ions: (a)  $[\text{Cr}(\text{CN})_6]^{4-}$ , (b)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ .
- 20.31** The absorption maximum for the complex ion  $[\text{Co}(\text{NH}_3)_6]^{3+}$  occurs at 470 nm. (a) Predict the

color of the complex and (b) calculate the crystal field splitting in kilojoules per mole.

- 20.32** A solution made by dissolving 0.875 g of  $\text{Co}(\text{NH}_3)_4\text{Cl}_3$  in 25.0 g of water freezes 0.56°C below the freezing point of pure water. Calculate the number of mole of ions produced when 1 mole of  $\text{Co}(\text{NH}_3)_4\text{Cl}_3$  is dissolved in water, and suggest a structure for the complex ion present in this compound.

## Reactions of Coordination Compounds

### Review Questions

- 20.33** Define the terms (a) labile complex, (b) inert complex.
- 20.34** Explain why a thermodynamically stable species may be chemically reactive and a thermodynamically unstable species may be unreactive.

### Problems

- 20.35** Oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , is sometimes used to clean rust stains from sinks and bathtubs. Explain the chemistry underlying this cleaning action.
- 20.36** The  $[\text{Fe}(\text{CN})_6]^{3-}$  complex is more labile than the  $[\text{Fe}(\text{CN})_6]^{4-}$  complex. Suggest an experiment that would prove that  $[\text{Fe}(\text{CN})_6]^{3-}$  is a labile complex.
- 20.37** Aqueous copper(II) sulfate solution is blue in color. When aqueous potassium fluoride is added, a green precipitate is formed. When aqueous potassium chloride is added instead, a bright-green solution is formed. Explain what is happening in these two cases.
- 20.38** When aqueous potassium cyanide is added to a solution of copper(II) sulfate, a white precipitate, soluble in an excess of potassium cyanide, is formed. No precipitate is formed when hydrogen sulfide is bubbled through the solution at this point. Explain.
- 20.39** A concentrated aqueous copper(II) chloride solution is bright green in color. When diluted with water, the solution becomes light blue. Explain.
- 20.40** In a dilute nitric acid solution,  $\text{Fe}^{3+}$  reacts with thiocyanate ion ( $\text{SCN}^-$ ) to form a dark-red complex:
- $$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{SCN}^- \rightleftharpoons \text{H}_2\text{O} + [\text{Fe}(\text{H}_2\text{O})_5\text{NCS}]^{2+}$$
- The equilibrium concentration of  $[\text{Fe}(\text{H}_2\text{O})_5\text{NCS}]^{2+}$  may be determined by how darkly colored the solution is (measured by a spectrometer). In one such experiment, 1.0 mL of 0.20 M  $\text{Fe}(\text{NO}_3)_3$  was mixed with 1.0 mL of  $1.0 \times 10^{-3}$  M KSCN and 8.0 mL of dilute  $\text{HNO}_3$ . The color of the solution quantitatively indicated that the  $[\text{Fe}(\text{H}_2\text{O})_5\text{NCS}]^{2+}$  concentration was  $7.3 \times 10^{-5}$  M. Calculate the formation constant for  $[\text{Fe}(\text{H}_2\text{O})_5\text{NCS}]^{2+}$ .

## Additional Problems

- 20.41** Explain these facts: (a) Copper and iron have several oxidation states, whereas zinc exists in only one.

(b) Copper and iron form colored ions, whereas zinc does not.

- 20.42** The formation constant for the reaction  $\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$  is  $1.5 \times 10^7$  and that for the reaction  $\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons [\text{Ag}(\text{CN})_2]^-$  is  $1.0 \times 10^{21}$  at  $25^\circ\text{C}$  (see Table 17.4). Calculate the equilibrium constant at  $25^\circ\text{C}$  for the reaction



- 20.43** Hemoglobin is the oxygen-carrying protein. In each hemoglobin molecule, there are four heme groups. In each heme group an Fe(II) ion is octahedrally bound to five N atoms and to either a water molecule (in deoxyhemoglobin) or an oxygen molecule (in oxyhemoglobin). Oxyhemoglobin is bright red, whereas deoxyhemoglobin is purple. Show that the difference in color can be accounted for qualitatively on the basis of high-spin and low-spin complexes. (*Hint:*  $\text{O}_2$  is a strong-field ligand.)

- 20.44** Hydrated  $\text{Mn}^{2+}$  ions are practically colorless (see Figure 20.15) even though they possess five  $3d$  electrons. Explain. (*Hint:* Electronic transitions in which there is a change in the number of unpaired electrons do not occur readily.)

- 20.45** Which of these hydrated cations are colorless:  $\text{Fe}^{2+}(aq)$ ,  $\text{Zn}^{2+}(aq)$ ,  $\text{Cu}^+(aq)$ ,  $\text{Cu}^{2+}(aq)$ ,  $\text{V}^{5+}(aq)$ ,  $\text{Ca}^{2+}(aq)$ ,  $\text{Co}^{2+}(aq)$ ,  $\text{Sc}^{3+}(aq)$ ,  $\text{Pb}^{2+}(aq)$ ? Explain your choice.

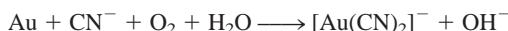
- 20.46** In each of these pairs of complexes, choose the one that absorbs light at a longer wavelength: (a)  $[\text{Co}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ; (b)  $[\text{FeF}_6]^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ; (c)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $[\text{CuCl}_4]^{2-}$ .

- 20.47** A student in 1895 prepared three chromium coordination compounds having the same formulas of  $\text{CrCl}_3(\text{H}_2\text{O})_6$  with these properties:

| Color       | $\text{Cl}^-$ Ions in Solution per Formula Unit |
|-------------|---|
| Violet      | 3   |
| Light green | 2   |
| Dark green  | 1   |

Write modern formulas for these compounds and suggest a method for confirming the number of  $\text{Cl}^-$  ions present in solution in each case. (*Hint:* Some of the compounds may exist as hydrates, which are compounds that have a specific number of water molecules attached to them. The Cr has a coordination number of 6 in all three compounds.)

- 20.48** Complex ion formation has been used to extract gold, which exists in nature in the uncombined state. To separate it from other solid impurities, the ore is treated with a sodium cyanide ( $\text{NaCN}$ ) solution in the presence of air to dissolve the gold by forming the soluble complex ion  $[\text{Au}(\text{CN})_2]^-$ . (a) Balance the following equation:



(b) The gold is obtained by reducing the complex ion with zinc metal. Write a balanced ionic equation for this process. (c) What is the geometry and coordination number of the  $[\text{Au}(\text{CN})_2]^-$  ion?

- 20.49** Aqueous solutions of  $\text{CoCl}_2$  are generally either light pink or blue. Low concentrations and low temperatures favor the pink form while high concentrations and high temperatures favor the blue form. Adding hydrochloric acid to a pink solution of  $\text{CoCl}_2$  causes the solution to turn blue; the pink color is restored by the addition of  $\text{HgCl}_2$ . Account for these observations.

- 20.50** Which is a stronger oxidizing agent,  $\text{Mn}^{3+}$  or  $\text{Cr}^{3+}$ ? Explain.

- 20.51** Suggest a method that would enable you to distinguish between *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  and *trans*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ .

- 20.52** The label of a certain brand of mayonnaise lists EDTA as a food preservative. How does EDTA prevent the spoilage of mayonnaise?

- 20.53** You are given two solutions containing  $\text{FeCl}_2$  and  $\text{FeCl}_3$  at the same concentration. One solution is light yellow and the other one is brown. Identify these solutions based only on color.

## SPECIAL PROBLEMS

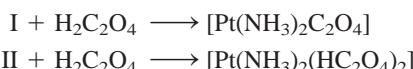
- 20.54** How many geometric isomers can the following square planar complex have?



- 20.55** Carbon monoxide binds to the iron atom in hemoglobin some 200 times more strongly than oxygen. This is the reason why CO is a toxic substance. The metal-to-ligand sigma bond is formed by donating a lone pair from the donor atom to an empty  $sp^3d^2$  orbital on Fe. (a) On the

basis of electronegativities, would you expect the C or O atom to form the bond to Fe? (b) Draw a diagram illustrating the overlap of the orbitals involved in bonding.

- 20.56**  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  is found to exist in two geometric isomers designated I and II, which react with oxalic acid as follows:



Comment on the structures of I and II.

- 20.57** The compound 1,1,1-trifluoroacetylacetone (tfa) is a bidentate ligand:



It forms a tetrahedral complex with  $\text{Be}^{2+}$  and a square planar complex with  $\text{Cu}^{2+}$ . Draw structures of these complex ions and identify the type of isomers exhibited by these ions.

- 20.58** Commercial silver-plating operations frequently use a solution containing the complex  $\text{Ag}(\text{CN})_2^-$  ion. Because the formation constant ( $K_f$ ) is quite large, this procedure ensures that the free  $\text{Ag}^+$  concentration in solution is low for uniform electrodeposition. In one process, a chemist added 9.0 L of 5.0 M NaCN to 90.0 L of 0.20 M  $\text{AgNO}_3$ . Calculate the concentration of free  $\text{Ag}^+$  ions at equilibrium. See Table 16.4 for  $K_f$  value.

- 20.59** Draw qualitative diagrams for the crystal-field splittings in (a) a linear complex ion  $\text{ML}_2$ , (b) a trigonal-planar complex ion  $\text{ML}_3$ , and (c) a trigonal-bipyramidal complex ion  $\text{ML}_5$ .

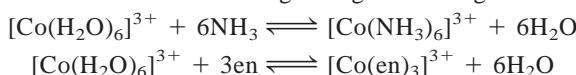
- 20.60** (a) The free  $\text{Cu}(\text{I})$  ion is unstable in solution and has a tendency to disproportionate:



Use the information in Table 19.1 (p. 651) to calculate the equilibrium constant for the reaction.

(b) Based on your result in (a), explain why most  $\text{Cu}(\text{I})$  compounds are insoluble.

- 20.61** Consider the following two ligand exchange reactions:



(a) Which of the reactions should have a larger  $\Delta S^\circ$ ?

(b) Given that the Co—N bond strength is approximately the same in both complexes, which reaction will have a larger equilibrium constant? Explain your choices.

- 20.62** Copper is also known to exist in +3 oxidation state, which is believed to be involved in some biological electron transfer reactions. (a) Would you expect this oxidation state of copper to be stable? Explain. (b) Name the compound  $\text{K}_3\text{CuF}_6$  and predict the geometry of the complex ion and its magnetic properties. (c) Most of the known  $\text{Cu}(\text{III})$  compounds have square planar geometry. Are these compounds diamagnetic or paramagnetic?

## ANSWERS TO PRACTICE EXERCISES

**20.1** K: +1; Au: +3.

**20.2** Tetraquaquadichlorochromium(III) chloride.

**20.3**  $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$ .    **20.4** 5.

# 21



A view of the Cygnus Loop supernova. When most of the fuel in a star is consumed, its core collapses and its outer layer explodes in a supernova. Elements through iron are formed in active stars and heavier elements are formed in supernovas.

## Nuclear Chemistry

### CHAPTER OUTLINE

- 21.1** The Nature of Nuclear Reactions 709  
Balancing Nuclear Equations
- 21.2** Nuclear Stability 711  
Nuclear Binding Energy
- 21.3** Natural Radioactivity 716  
Kinetics of Radioactive Decay • Dating Based on Radioactive Decay
- 21.4** Nuclear Transmutation 720  
The Transuranium Elements
- 21.5** Nuclear Fission 722  
The Atomic Bomb • Nuclear Reactors
- 21.6** Nuclear Fusion 727  
Fusion Reactors • The Hydrogen Bomb
- 21.7** Uses of Isotopes 729  
Structural Determination • Study of Photosynthesis • Isotopes in Medicine
- 21.8** Biological Effects of Radiation 732



### Interactive Activity Summary

1. Animation: Radioactive Decay (21.3)
2. Animation: Nuclear Fission (21.5)

### ESSENTIAL CONCEPTS

**Nuclear Stability** To maintain nuclear stability, the ratio of neutrons-to-protons must fall within a certain range. A quantitative measure of nuclear stability is nuclear binding energy, which is the energy required to break up a nucleus into its component protons and neutrons. Nuclear binding energy can be calculated from the masses of protons and neutrons and that of the nucleus using Einstein's mass-energy equivalence relationship.

**Natural Radioactivity and Nuclear Transmutation** Unstable nuclei undergo spontaneous decay with the emission of radiation and particles. All nuclear decays obey first-order kinetics. The half-lives of several radioactive nuclei have been used to date objects. Stable nuclei can also be made radioactive by bombardment with elementary particles or atomic nuclei. Many new elements have been created artificially in particle accelerators where such bombardments occur.

**Nuclear Fission and Nuclear Fusion** Certain nuclei, when bombarded with neutrons, undergo fission to produce smaller nuclei, additional neutrons, and a large amount of energy. When enough nuclei are present to reach critical mass, a nuclear chain reaction, a self-sustaining sequence of nuclear fission reactions, takes place. Nuclear fissions find applications in the construction of atomic bombs and nuclear reactors. Nuclear fusion is the process in which nuclei of light elements are made to fuse at very high temperatures to form a heavier nucleus. Such a process releases even a greater amount of energy than nuclear fission and is used in making hydrogen, or thermonuclear, bombs.

**Uses of Isotopes** Isotopes, especially radioactive isotopes, are used as tracers to study the mechanisms of chemical and biological reactions and as medical diagnostic tools.

**Biological Effects of Radiation** The penetrating and harmful effects of radiation on biological systems have been thoroughly studied and are well understood.

## 21.1 The Nature of Nuclear Reactions

With the exception of hydrogen ( $^1\text{H}$ ), all nuclei contain two kinds of fundamental particles, called *protons* and *neutrons*. Some nuclei are unstable; they emit particles and/or electromagnetic radiation spontaneously (see Section 2.2). The name for this phenomenon is *radioactivity*. All elements having an atomic number greater than 83 are radioactive. For example, the isotope of polonium, polonium-210 ( $^{210}_{84}\text{Po}$ ), decays spontaneously to  $^{206}_{82}\text{Pb}$  by emitting an  $\alpha$  particle.

Another type of radioactivity, known as *nuclear transmutation*, results from the bombardment of nuclei by neutrons, protons, or other nuclei. An example of a nuclear transmutation is the conversion of atmospheric  $^{14}\text{N}$  to  $^{14}\text{C}$  and  $^1\text{H}$ , which results when the nitrogen isotope captures a neutron (from the sun). In some cases, heavier elements are synthesized from lighter elements. This type of transmutation occurs naturally in outer space, but it can also be achieved artificially, as we will see in Section 21.4.

Radioactive decay and nuclear transmutation are *nuclear reactions*, which differ significantly from ordinary chemical reactions. Table 21.1 summarizes the differences.

### Balancing Nuclear Equations

To discuss nuclear reactions in any depth, we need to understand how to write and balance the equations. Writing a nuclear equation differs somewhat from writing equations for chemical reactions. In addition to writing the symbols for various chemical elements, we must also explicitly indicate protons, neutrons, and electrons. In fact, we must show the numbers of protons and neutrons present in *every* species in such an equation.

The symbols for elementary particles are as follows:

|                              |              |                             |                             |                             |
|------------------------------|--------------|-----------------------------|-----------------------------|-----------------------------|
| $^1\text{p}$ or $^1\text{H}$ | $^0\text{n}$ | $^-_1\text{e}$ or $^0\beta$ | $^+_1\text{e}$ or $^0\beta$ | $^4\text{He}$ or $^4\alpha$ |
| proton                       | neutron      | electron                    | positron                    | $\alpha$ particle           |

In accordance with the notation used in Section 2.3, the superscript in each case denotes the mass number (the total number of neutrons and protons present) and the subscript is the atomic number (the number of protons). Thus, the “atomic number” of a proton is 1, because there is one proton present, and the “mass number” is

**TABLE 21.1 Comparison of Chemical Reactions and Nuclear Reactions**

| Chemical Reactions   | Nuclear Reactions   |
|--|---|
| 1. Atoms are rearranged by the breaking and forming of chemical bonds.                               | 1. Elements (or isotopes of the same elements) are converted from one to another.       |
| 2. Only electrons in atomic or molecular orbitals are involved in the breaking and forming of bonds. | 2. Protons, neutrons, electrons, and other elementary particles may be involved.        |
| 3. Reactions are accompanied by absorption or release of relatively small amounts of energy.         | 3. Reactions are accompanied by absorption or release of tremendous amounts of energy.  |
| 4. Rates of reaction are influenced by temperature, pressure, concentration, and catalysts.          | 4. Rates of reaction normally are not affected by temperature, pressure, and catalysts. |

also 1, because there is one proton but no neutrons present. On the other hand, the “mass number” of a neutron is 1, but its “atomic number” is zero, because there are no protons present. For the electron, the “mass number” is zero (there are neither protons nor neutrons present), but the “atomic number” is  $-1$ , because the electron possesses a unit negative charge.

The symbol  ${}^0_1e$  represents an electron in or from an atomic orbital. The symbol  ${}^0_{-1}\beta$  represents an electron that, although physically identical to any other electron, comes from a nucleus (in a decay process in which a neutron is converted to a proton and an electron) and not from an atomic orbital. The **positron** has the same mass as the electron, but bears a  $+1$  charge. The  $\alpha$  particle has two protons and two neutrons, so its atomic number is 2 and its mass number is 4.

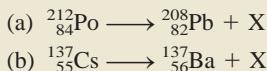
In balancing any nuclear equation, we observe these rules:

- The total number of protons plus neutrons in the products and in the reactants must be the same (conservation of mass number).
- The total number of nuclear charges in the products and in the reactants must be the same (conservation of atomic number).

If we know the atomic numbers and mass numbers of all the species but one in a nuclear equation, we can identify the unknown species by applying these rules, as shown in Example 21.1, which illustrates how to balance nuclear decay equations.

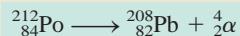
### Example 21.1

Balance the following nuclear equations (that is, identify the product X):

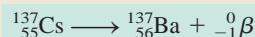


**Strategy** In balancing nuclear equations, note that the sum of atomic numbers and that of mass numbers must match on both sides of the equation.

**Solution** (a) The mass number and atomic number are 212 and 84, respectively, on the left-hand side and 208 and 82, respectively, on the right-hand side. Thus, X must have a mass number of 4 and an atomic number of 2, which means that it is an  $\alpha$  particle. The balanced equation is



(b) In this case, the mass number is the same on both sides of the equation, but the atomic number of the product is 1 more than that of the reactant. Thus, X must have a mass number of 0 and an atomic number of  $-1$ , which means that it is a  $\beta$  particle. The only way this change can come about is to have a neutron in the Cs nucleus transformed into a proton and an electron; that is,  ${}^0_0\text{n} \longrightarrow {}^1_1\text{p} + {}^0_{-1}\beta$  (note that this process does not alter the mass number). Thus, the balanced equation is



We use the  ${}^0_{-1}\beta$  notation here because the electron came from the nucleus.

Similar problems: 21.5, 21.6.

**Check** Note that the equation in (a) and (b) are balanced for nuclear particles but not for electrical charges. To balance the charges, we would need to add two electrons on the right-hand side of (a) and express barium as a cation ( $\text{Ba}^+$ ) in (b).

**Practice Exercise** Identify X in the following nuclear equation:



## 21.2 Nuclear Stability

The nucleus occupies a very small portion of the total volume of an atom, but it contains most of the atom's mass because both the protons and the neutrons reside there. In studying the stability of the atomic nucleus, it is helpful to know something about its density, because it tells us how tightly the particles are packed together. As a sample calculation, let us assume that a nucleus has a radius of  $5 \times 10^{-3}$  pm and a mass of  $1 \times 10^{-22}$  g. These figures correspond roughly to a nucleus containing 30 protons and 30 neutrons. Density is mass/volume, and we can calculate the volume from the known radius (the volume of a sphere is  $\frac{4}{3}\pi r^3$ , where  $r$  is the radius of the sphere). First we convert the pm units to cm. Then we calculate the density in g/cm<sup>3</sup>:

$$r = 5 \times 10^{-3} \text{ pm} \times \frac{1 \times 10^{-12} \text{ m}}{1 \text{ pm}} \times \frac{100 \text{ cm}}{1 \text{ m}} = 5 \times 10^{-13} \text{ cm}$$

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{1 \times 10^{-22} \text{ g}}{\frac{4}{3}\pi r^3} = \frac{1 \times 10^{-22} \text{ g}}{\frac{4}{3}\pi(5 \times 10^{-13} \text{ cm})^3}$$

$$= 2 \times 10^{14} \text{ g/cm}^3$$

This is an exceedingly high density. The highest density known for an element is 22.6 g/cm<sup>3</sup>, for osmium (Os). Thus, the average atomic nucleus is roughly  $9 \times 10^{12}$  (or 9 trillion) times more dense than the densest element known!

To dramatize the almost incomprehensibly high density, it has been suggested that it is equivalent to packing the mass of all the world's automobiles into one thimble.

The enormously high density of the nucleus prompts us to wonder what holds the particles together so tightly. From electrostatic interaction we know that like charges repel and unlike charges attract one another. We would thus expect the protons to repel one another strongly, particularly when we consider how close they must be to each other. This indeed is so. However, in addition to the repulsion, there are also short-range attractions between proton and proton, proton and neutron, and neutron and neutron. The stability of any nucleus is determined by the difference between electrostatic repulsion and the short-range attraction. If repulsion outweighs attraction, the nucleus disintegrates, emitting particles and/or radiation. If attractive forces prevail, the nucleus is stable.

The principal factor that determines whether a nucleus is stable is the *neutron-to-proton ratio* (*n/p*). For stable atoms of elements having low atomic number, the *n/p* value is close to 1. As the atomic number increases, the neutron-to-proton ratios of the stable nuclei become greater than 1. This deviation at higher atomic numbers arises because a larger number of neutrons is needed to counteract the strong repulsion among the protons and stabilize the nucleus. The following rules are useful in predicting nuclear stability:

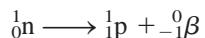
1. Nuclei that contain 2, 8, 20, 50, 82, or 126 protons or neutrons are generally more stable than nuclei that do not possess these numbers. For example, there are 10 stable isotopes of tin (Sn) with the atomic number 50 and only 2 stable isotopes of antimony (Sb) with the atomic number 51. The numbers 2, 8, 20, 50, 82, and 126 are called *magic numbers*. The significance of these numbers for nuclear stability is similar to the numbers of electrons associated with the very stable noble gases (that is, 2, 10, 18, 36, 54, and 86 electrons).
2. Nuclei with even numbers of both protons and neutrons are generally more stable than those with odd numbers of these particles (Table 21.2).
3. All isotopes of the elements with atomic numbers higher than 83 are radioactive. All isotopes of technetium (Tc,  $Z = 43$ ) and promethium (Pm,  $Z = 61$ ) are radioactive.

Figure 21.1 shows a plot of the number of neutrons versus the number of protons in various isotopes. The stable nuclei are located in an area of the graph known as the

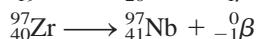
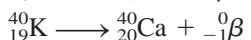
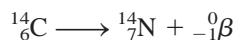
**TABLE 21.2****Number of Stable Isotopes with Even and Odd Numbers of Protons and Neutrons**

| Protons | Neutrons | Number of Stable Isotopes |
|---------|----------|---------------------------|
| Odd     | Odd      | 4                         |
| Odd     | Even     | 50                        |
| Even    | Odd      | 53                        |
| Even    | Even     | 164                       |

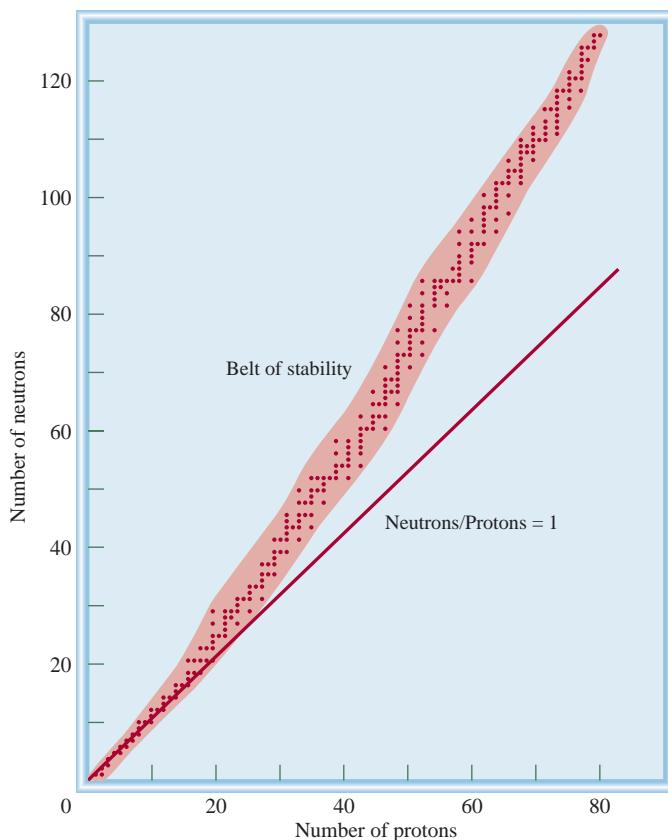
*belt of stability.* Most radioactive nuclei lie outside this belt. Above the stability belt, the nuclei have higher neutron-to-proton ratios than those within the belt (for the same number of protons). To lower this ratio (and hence move down toward the belt of stability), these nuclei undergo the following process, called  *$\beta$ -particle emission*:



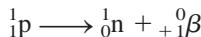
Beta-particle emission leads to an increase in the number of protons in the nucleus and a simultaneous decrease in the number of neutrons. Some examples are

**Figure 21.1**

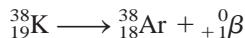
Plot of neutrons versus protons for various stable isotopes, represented by dots. The straight line represents the points at which the neutron-to-proton ratio equals 1. The shaded area represents the belt of stability.



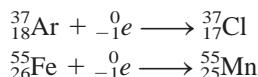
Below the stability belt, the nuclei have lower neutron-to-proton ratios than those in the belt (for the same number of protons). To increase this ratio (and hence move up toward the belt of stability), these nuclei either emit a positron



or undergo electron capture. An example of positron emission is



*Electron capture* is the capture of an electron—usually a 1s electron—by the nucleus. The captured electron combines with a proton to form a neutron so that the atomic number decreases by one while the mass number remains the same. This process has the same net effect as positron emission:



We use  ${}_{-1}^{0}e$  rather than  ${}_{+1}^{0}\beta$  here because the electron came from an atomic orbital and not from the nucleus.

## Nuclear Binding Energy

A quantitative measure of nuclear stability is the *nuclear binding energy*, which is the energy required to break up a nucleus into its component protons and neutrons. This quantity represents the conversion of mass to energy that occurs during an exothermic nuclear reaction.

The concept of nuclear binding energy evolved from studies of nuclear properties showing that the masses of nuclei are always less than the sum of the masses of the *nucleons*, which is a general term for the protons and neutrons in a nucleus. For example, the  ${}_{9}^{19}\text{F}$  isotope has an atomic mass of 18.9984 amu. The nucleus has 9 protons and 10 neutrons and therefore a total of 19 nucleons. Using the known masses of the  ${}_{1}^{1}\text{H}$  atom (1.007825 amu) and the neutron (1.008665 amu), we can carry out the following analysis. The mass of 9  ${}_{1}^{1}\text{H}$  atoms (that is, the mass of 9 protons and 9 electrons) is

$$9 \times 1.007825 \text{ amu} = 9.070425 \text{ amu}$$

and the mass of 10 neutrons is

$$10 \times 1.008665 \text{ amu} = 10.08665 \text{ amu}$$

Therefore, the atomic mass of a  ${}_{9}^{19}\text{F}$  atom calculated from the known numbers of electrons, protons, and neutrons is

$$9.070425 \text{ amu} + 10.08665 \text{ amu} = 19.15708 \text{ amu}$$

which is larger than 18.9984 amu (the measured mass of  ${}_{9}^{19}\text{F}$ ) by 0.1587 amu.

The difference between the mass of an atom and the sum of the masses of its protons, neutrons, and electrons is called the *mass defect*. Relativity theory tells us that the loss in mass shows up as energy (heat) given off to the surroundings. Thus, the formation of  ${}_{9}^{19}\text{F}$  is exothermic. Einstein's *mass-energy equivalence relationship* states that

$$E = mc^2 \quad (21.1)$$

This is the only equation listed in the Bartlett's quotations.

where  $E$  is energy,  $m$  is mass, and  $c$  is the speed of light. We can calculate the amount of energy released by writing

$$\Delta E = (\Delta m)c^2 \quad (21.2)$$

where  $\Delta E$  and  $\Delta m$  are defined as follows:

$$\begin{aligned}\Delta E &= \text{energy of product} - \text{energy of reactants} \\ \Delta m &= \text{mass of product} - \text{mass of reactants}\end{aligned}$$

Thus, for the change in mass we have

$$\begin{aligned}\Delta m &= 18.9984 \text{ amu} - 19.15708 \text{ amu} \\ &= -0.1587 \text{ amu}\end{aligned}$$

Because  ${}^{19}_9\text{F}$  has a mass that is less than the mass calculated from the number of electrons and nucleons present,  $\Delta m$  is a negative quantity. Consequently,  $\Delta E$  is also a negative quantity; that is, energy is released to the surroundings as a result of the formation of the fluorine-19 nucleus. So we calculate  $\Delta E$  as follows:

$$\begin{aligned}\Delta E &= (-0.1587 \text{ amu})(3.00 \times 10^8 \text{ m/s})^2 \\ &= -1.43 \times 10^{16} \text{ amu m}^2/\text{s}^2\end{aligned}$$

With the conversion factors

$$\begin{aligned}1 \text{ kg} &= 6.022 \times 10^{26} \text{ amu} \\ 1 \text{ J} &= 1 \text{ kg m}^2/\text{s}^2\end{aligned}$$

we obtain

$$\begin{aligned}\Delta E &= \left(-1.43 \times 10^{16} \frac{\text{amu} \cdot \text{m}^2}{\text{s}^2}\right) \times \left(\frac{1.00 \text{ kg}}{6.022 \times 10^{26} \text{ amu}}\right) \times \left(\frac{1 \text{ J}}{1 \text{ kg m}^2/\text{s}^2}\right) \\ &= -2.37 \times 10^{-11} \text{ J}\end{aligned}$$

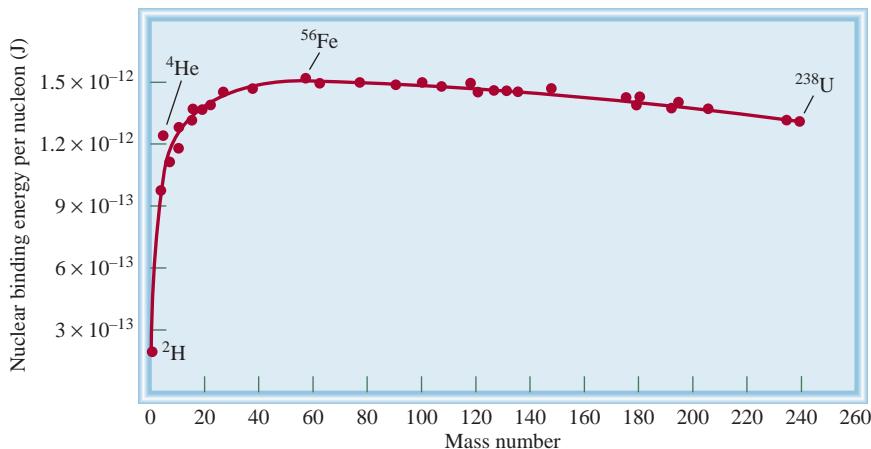
This is the amount of energy released when one fluorine-19 nucleus is formed from 9 protons and 10 neutrons. The nuclear binding energy of the nucleus is  $2.37 \times 10^{-11} \text{ J}$ , which is the amount of energy needed to decompose the nucleus into separate protons and neutrons. In the formation of 1 mole of fluorine nuclei, for instance, the energy released is

$$\begin{aligned}\Delta E &= (-2.37 \times 10^{-11} \text{ J})(6.022 \times 10^{23}/\text{mol}) \\ &= -1.43 \times 10^{13} \text{ J/mol} \\ &= -1.43 \times 10^{10} \text{ kJ/mol}\end{aligned}$$

The nuclear binding energy, therefore, is  $1.43 \times 10^{10} \text{ kJ}$  for 1 mole of fluorine-19 nuclei, which is a tremendously large quantity when we consider that the enthalpies of ordinary chemical reactions are of the order of only 200 kJ. The procedure we have followed can be used to calculate the nuclear binding energy of any nucleus.

As we have noted, nuclear binding energy is an indication of the stability of a nucleus. However, in comparing the stability of any two nuclei we must account for the fact that they have different numbers of nucleons. For this reason it is more meaningful to use the *nuclear binding energy per nucleon*, defined as

$$\text{nuclear binding energy per nucleon} = \frac{\text{nuclear binding energy}}{\text{number of nucleons}} \quad (21.3)$$



**Figure 21.2**  
Plot of nuclear binding energy per nucleon versus mass number.

For the fluorine-19 nucleus,

$$\begin{aligned} \text{nuclear binding energy per nucleon} &= \frac{2.37 \times 10^{-11} \text{ J}}{19 \text{ nucleons}} \\ &= 1.25 \times 10^{-12} \text{ J/nucleon} \end{aligned}$$

The nuclear binding energy per nucleon enables us to compare the stability of all nuclei on a common basis. Figure 21.2 shows the variation of nuclear binding energy per nucleon plotted against mass number. As you can see, the curve rises rather steeply. The highest binding energies per nucleon belong to elements with intermediate mass numbers—between 40 and 100—and are greatest for elements in the iron, cobalt, and nickel region (the Group 8B elements) of the periodic table. This means that the *net* attractive forces among the particles (protons and neutrons) are greatest for the nuclei of these elements.

### Example 21.2

The atomic mass of  $^{127}_{53}\text{I}$  is 126.9004 amu. Calculate the nuclear binding energy of this nucleus and the corresponding nuclear binding energy per nucleon.

**Strategy** To calculate the nuclear binding energy, we first determine the difference between the mass of the nucleus and the mass of all the protons and neutrons, which gives us the mass defect. Next, we apply Einstein's mass-energy relationship [ $\Delta E = (\Delta m)c^2$ ].

**Solution** There are 53 protons and 74 neutrons in the iodine nucleus. The mass of 53  $^1\text{H}$  atoms is

$$53 \times 1.007825 \text{ amu} = 53.41473 \text{ amu}$$

and the mass of 74 neutrons is

$$74 \times 1.008665 \text{ amu} = 74.64121 \text{ amu}$$

(Continued)

Therefore, the predicted mass for  $^{127}\text{I}$  is  $53.41473 + 74.64121 = 128.05594$  amu, and the mass defect is

$$\begin{aligned}\Delta m &= 126.9004 \text{ amu} - 128.05594 \text{ amu} \\ &= -1.1555 \text{ amu}\end{aligned}$$

The energy released is

$$\begin{aligned}\Delta E &= (\Delta m)c^2 \\ &= (-1.1555 \text{ amu})(3.00 \times 10^8 \text{ m/s})^2 \\ &= -1.04 \times 10^{17} \text{ amu} \cdot \text{m}^2/\text{s}^2\end{aligned}$$

Let's convert to a more familiar energy unit of joules. Recall that  $1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$ . Therefore, we need to convert amu to kg:

$$\begin{aligned}\Delta E &= -1.04 \times 10^{17} \frac{\text{amu} \cdot \text{m}^2}{\text{s}^2} \times \frac{1.00 \text{ g}}{6.022 \times 10^{23} \text{ amu}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \\ &= -1.73 \times 10^{-10} \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2} = -1.73 \times 10^{-10} \text{ J}\end{aligned}$$

**The neutron-to-proton ratio is 1.4, which places iodine-127 in the belt of stability.**

**Similar problems:** 21.19, 21.20.

Thus, the nuclear binding energy is  $1.73 \times 10^{-10} \text{ J}$ . The nuclear binding energy per nucleon is obtained as follows:

$$\frac{1.73 \times 10^{-10} \text{ J}}{127 \text{ nucleons}} = 1.36 \times 10^{-12} \text{ J/nucleon}$$

**Practice Exercise** Calculate the nuclear binding energy (in J) and the nuclear binding energy per nucleon of  $^{209}_{83}\text{Bi}$  (208.9804 amu).

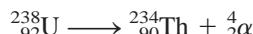


## 21.3 Natural Radioactivity

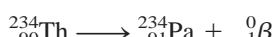
Nuclei outside the belt of stability, as well as nuclei with more than 83 protons, tend to be unstable. The spontaneous emission by unstable nuclei of particles or electromagnetic radiation, or both, is known as radioactivity. The main types of radiation are:  $\alpha$  particles (or doubly charged helium nuclei,  $\text{He}^{2+}$ );  $\beta$  particles (or electrons);  $\gamma$  rays, which are very-short-wavelength ( $0.1 \text{ nm}$  to  $10^{-4} \text{ nm}$ ) electromagnetic waves; positron emission; and electron capture.

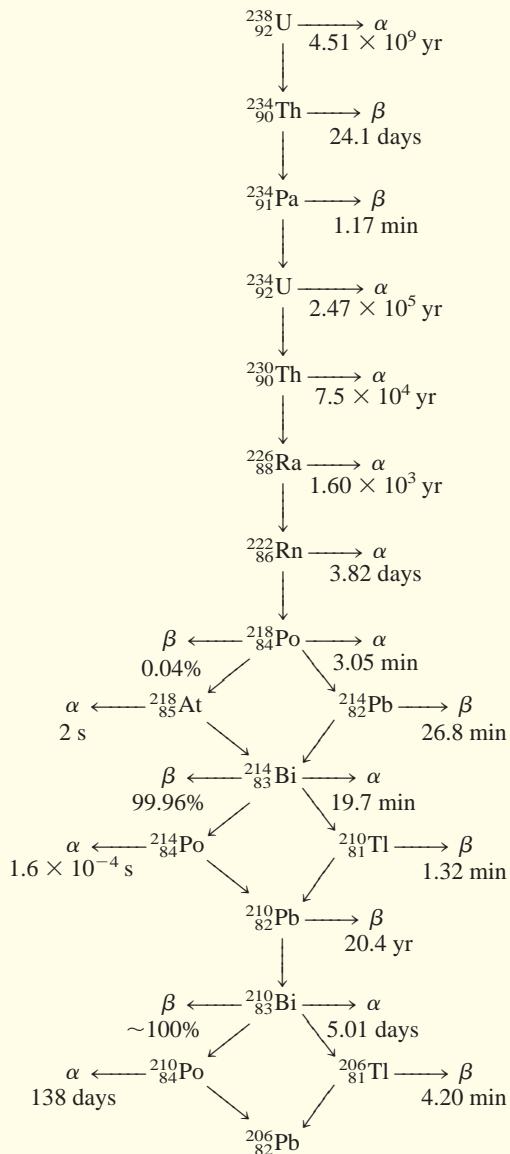
The disintegration of a radioactive nucleus is often the beginning of a *radioactive decay series*, which is *a sequence of nuclear reactions that ultimately result in the formation of a stable isotope*. Table 21.3 shows the decay series of naturally occurring uranium-238, which involves 14 steps. This decay scheme, known as the *uranium decay series*, also shows the half-lives of all the products.

It is important to be able to balance the equation of a nuclear reaction for each of the steps in a radioactive decay series. For example, the first step in the uranium decay series is the decay of uranium-238 to thorium-234, with the emission of an  $\alpha$  particle. Hence, the reaction is



The next step is represented by



**TABLE 21.3** The Uranium Decay Series\*

\*The times denote the half-lives.

and so on. In a discussion of radioactive decay steps, the beginning radioactive isotope is called the *parent* and the product, the *daughter*.

## Kinetics of Radioactive Decay

All radioactive decays obey first-order kinetics. Therefore, the rate of radioactive decay at any time  $t$  is given by

$$\text{rate of decay at time } t = \lambda N$$

where  $\lambda$  is the first-order rate constant and  $N$  is the number of radioactive nuclei present at time  $t$ . (We use  $\lambda$  instead of  $k$  for rate constant in accord with the notation used by nuclear scientists.) According to Equation (14.3), the number of radioactive nuclei at time zero ( $N_0$ ) and time  $t$  ( $N_t$ ) are given by

$$\ln \frac{N_t}{N_0} = -\lambda t$$

and the corresponding half-life of the reaction is given by Equation (14.5):

$$t_{\frac{1}{2}} = \frac{0.693}{\lambda}$$

We do not have to wait  $4.51 \times 10^9$  yr to make a half-life measurement of uranium-238. Its value can be calculated from the rate constant using Equation (14.5).

The half-lives (hence the rate constants) of radioactive isotopes vary greatly from nucleus to nucleus. For example, looking at Table 21.3, we find two extreme cases:



The ratio of these two rate constants after conversion to the same time unit is about  $1 \times 10^{21}$ , an enormously large number. Furthermore, the rate constants are unaffected by changes in environmental conditions such as temperature and pressure. These highly unusual features are not seen in ordinary chemical reactions (see Table 21.1).

## Dating Based on Radioactive Decay

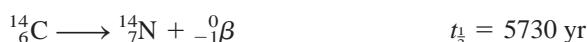
The half-lives of radioactive isotopes have been used as “atomic clocks” to determine the ages of certain objects. Some examples of dating by radioactive decay measurements will be described here.

### Radiocarbon Dating

The carbon-14 isotope is produced when atmospheric nitrogen is bombarded by cosmic rays:



The radioactive carbon-14 isotope decays according to the equation



The carbon-14 isotopes enter the biosphere as  $\text{CO}_2$ , which is taken up in plant photosynthesis. Plant-eating animals in turn exhale carbon-14 in  $\text{CO}_2$ . Eventually, carbon-14 participates in many aspects of the carbon cycle. The  ${}^{14}\text{C}$  lost by radioactive decay is constantly replenished by the production of new isotopes in the atmosphere until a dynamic equilibrium is established whereby the ratio of  ${}^{14}\text{C}$  to  ${}^{12}\text{C}$  remains constant in living matter. But when an individual plant or an animal dies, the carbon-14 isotope in it is no longer replenished, so the ratio decreases as  ${}^{14}\text{C}$  decays. This same change occurs when carbon atoms are trapped in coal, petroleum, or wood preserved underground, and in mummified bodies. After a number of years, there are proportionately fewer  ${}^{14}\text{C}$  nuclei in a mummy than in a living person.

The decreasing ratio of  ${}^{14}\text{C}$  to  ${}^{12}\text{C}$  can be used to estimate the age of a specimen. Using Equation (14.3), we can write

$$\ln \frac{N_0}{N_t} = \lambda t$$



The age of the Shroud of Turin was shown by carbon-14 dating to be between A.D. 1260 and A.D. 1390, and therefore the shroud cannot be the burial cloth of Jesus Christ.

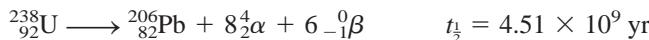
in which  $N_0$  and  $N_t$  are the number of  $^{14}\text{C}$  nuclei present at  $t = 0$  and  $t = t$ , and  $\lambda$  is the first-order rate constant ( $1.21 \times 10^{-4} \text{ yr}^{-1}$ ). Because the decay rate is proportional to the amount of the radioactive isotope present, we have

$$\begin{aligned} t &= \frac{1}{\lambda} \ln \frac{N_0}{N_t} \\ &= \frac{1}{1.21 \times 10^{-4} \text{ yr}^{-1}} \ln \frac{\text{decay rate of fresh sample}}{\text{decay rate of old sample}} \end{aligned}$$

Thus, by measuring the decay rates of the fresh sample and the old sample, we can calculate  $t$ , which is the age of the old sample. Radiocarbon dating is a valuable tool for estimating the age of objects (containing C atoms) dating back 1000 to 50,000 years.

### Dating Using Uranium-238 Isotopes

Because some of the intermediate products in the uranium decay series have very long half-lives (see Table 21.3), this series is particularly suitable for estimating the age of rocks in the earth and of extraterrestrial objects. The half-life for the first step ( $^{238}_{92}\text{U}$  to  $^{234}_{90}\text{Th}$ ) is  $4.51 \times 10^9 \text{ yr}$ . This is about 20,000 times the second largest value (that is,  $2.47 \times 10^5 \text{ yr}$ ), which is the half-life for  $^{234}_{92}\text{U}$  to  $^{230}_{90}\text{Th}$ . Therefore, as a good approximation, we can assume that the half-life for the overall process (that is, from  $^{238}_{92}\text{U}$  to  $^{206}_{82}\text{Pb}$ ) is governed solely by the first step:



In naturally occurring uranium minerals, we should and do find some lead-206 isotopes formed by radioactive decay. Assuming that no lead was present when the mineral was formed and that the mineral has not undergone chemical changes that would enable the lead-206 isotope to be separated from the parent uranium-238, it is possible to estimate the age of the rocks from the mass ratio of  $^{206}_{82}\text{Pb}$  to  $^{238}_{92}\text{U}$ . The preceding equation tells us that for every mole, or 238 g, of uranium that undergoes complete decay, 1 mole, or 206 g, of lead is formed. If only half a mole of uranium-238 has undergone decay, the mass ratio  $^{206}\text{Pb}/^{238}\text{U}$  becomes

$$\frac{206 \text{ g}/2}{238 \text{ g}/2} = 0.866$$

and the process would have taken a half-life of  $4.51 \times 10^9 \text{ yr}$  to complete (Figure 21.3). Ratios lower than 0.866 mean that the rocks are less than  $4.51 \times 10^9 \text{ yr}$  old, and higher ratios suggest a greater age. Interestingly, studies based on the uranium series as well as other decay series put the age of the oldest rocks and, therefore, probably the age of Earth itself at  $4.5 \times 10^9$ , or 4.5 billion, years.

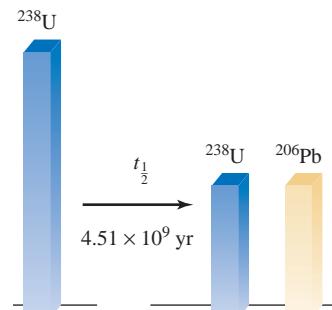
### Dating Using Potassium-40 Isotopes

This is one of the most important techniques employed in geochemistry. The radioactive potassium-40 isotope decays by several different modes, but the relevant one as far as dating is concerned is that of electron capture:



The accumulation of gaseous argon-40 is used to gauge the age of a specimen. When a potassium-40 atom in a mineral decays, argon-40 is trapped in the lattice of the mineral and can escape only if the material is melted. Melting, therefore, is the procedure for

We can think of the first step as the rate-determining step in the overall process.



**Figure 21.3**

After one half-life, half of the original uranium-238 is converted to lead-206.

analyzing a mineral sample in the laboratory. The amount of argon-40 present can be conveniently measured with a mass spectrometer (see p. 66). Knowing the ratio of argon-40 to potassium-40 in the mineral and the half-life of decay makes it possible to establish the ages of rocks ranging from millions to billions of years old.

## 21.4 Nuclear Transmutation

The scope of nuclear chemistry would be rather narrow if study were limited to natural radioactive elements. An experiment performed by Rutherford in 1919, however, suggested the possibility of producing radioactivity artificially. When he bombarded a sample of nitrogen with  $\alpha$  particles, the following reaction took place:



An oxygen-17 isotope was produced with the emission of a proton. This reaction demonstrated for the first time the feasibility of converting one element into another, by the process of nuclear transmutation. Nuclear transmutation differs from radioactive decay in that the former is brought about by the collision of two particles.

The preceding reaction can be abbreviated as  ${}^{14}_{\text{7}}\text{N}(\alpha, \text{p}) {}^{17}_{\text{8}}\text{O}$ . Note that in the parentheses the bombarding particle is written first, followed by the ejected particle.

### Example 21.3

Write the balanced equation for the nuclear reaction  ${}^{56}_{\text{26}}\text{Fe}(\text{d}, \alpha) {}^{54}_{\text{25}}\text{Mn}$ , where d represents the deuterium nucleus (that is,  ${}^2_1\text{H}$ ).

**Strategy** To write the balanced nuclear equation, remember that the first isotope  ${}^{56}_{\text{26}}\text{Fe}$  is the reactant and the second isotope  ${}^{54}_{\text{25}}\text{Mn}$  is the product. The first symbol in parentheses (d) is the bombarding particle and the second symbol in parentheses ( $\alpha$ ) is the particle emitted as a result of nuclear transmutation.

**Solution** The abbreviation tells us that when iron-56 is bombarded with a deuterium nucleus, it produces the manganese-54 nucleus plus an  $\alpha$  particle,  ${}^4_2\text{He}$ . Thus, the equation for this reaction is



**Check** Make sure that the sum of mass numbers and the sum of atomic numbers are the same on both sides of the equation.

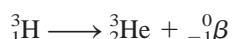
**Practice Exercise** Write a balanced equation for  ${}^{106}_{\text{46}}\text{Pd}(\alpha, \text{p}) {}^{109}_{\text{47}}\text{Ag}$ .

Similar problems: 21.33, 21.34.

Although light elements are generally not radioactive, they can be made so by bombarding their nuclei with appropriate particles. As we saw earlier, the radioactive carbon-14 isotope can be prepared by bombarding nitrogen-14 with neutrons. Tritium,  ${}^3_1\text{H}$ , is prepared according to the following bombardment:



Tritium decays with the emission of  $\beta$  particles:



$$t_{\frac{1}{2}} = 12.5 \text{ yr}$$

Many synthetic isotopes are prepared by using neutrons as projectiles. This approach is particularly convenient because neutrons carry no charges and therefore are not repelled by the targets—the nuclei. In contrast, when the projectiles are positively charged particles (for example, protons or  $\alpha$  particles), they must have considerable kinetic energy to overcome the electrostatic repulsion between themselves and the target nuclei. The synthesis of phosphorus from aluminum is one example:

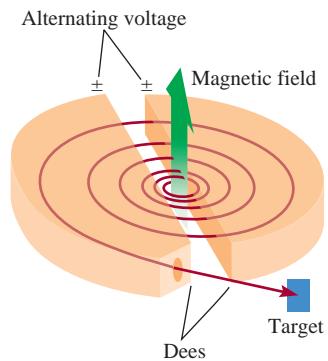


A *particle accelerator* uses electric and magnetic fields to increase the kinetic energy of charged species so that a reaction will occur (Figure 21.4). Alternating the polarity (that is, + and −) on specially constructed plates causes the particles to accelerate along a spiral path. When they have the energy necessary to initiate the desired nuclear reaction, they are guided out of the accelerator into a collision with a target substance.

Various designs have been developed for particle accelerators, one of which accelerates particles along a linear path of about 3 km (Figure 21.5). It is now possible to accelerate particles to a speed well above 90 percent of the speed of light. (According to Einstein's theory of relativity, it is impossible for a particle to move *at* the speed of light. The only exception is the photon, which has a zero rest mass.) The extremely energetic particles produced in accelerators are employed by physicists to smash atomic nuclei to fragments. Studying the debris from such disintegrations provides valuable information about nuclear structure and binding forces.

## The Transuranium Elements

Particle accelerators made it possible to synthesize the so-called **transuranium elements**, *elements with atomic numbers greater than 92*. Neptunium ( $Z = 93$ ) was first prepared in 1940. Since then, 22 other transuranium elements have been synthesized. All isotopes of these elements are radioactive. Table 21.4 lists the transuranium elements up to  $Z = 109$  and the reactions through which they are formed.



**Figure 21.4**  
Schematic diagram of a cyclotron particle accelerator. The particle (an ion) to be accelerated starts at the center and is forced to move in a spiral path through the influence of electric and magnetic fields until it emerges at a high velocity. The magnetic fields are perpendicular to the plane of the dees (so-called because of their shape), which are hollow and serve as electrodes.



**Figure 21.5**  
A section of a particle accelerator.

**TABLE 21.4** The Transuranium Elements

| Atomic Number | Name          | Symbol | Preparation   | Half-life |
|---------------|---------------|--------|---|-----------|
| 93            | Neptunium     | Np     | $^{238}_{92}\text{U} + {}^1_0\text{n} \longrightarrow {}^{239}_{93}\text{Np} + {}^0_{-1}\beta$            | 2.4 d     |
| 94            | Plutonium     | Pu     | ${}^{239}_{93}\text{Np} \longrightarrow {}^{239}_{94}\text{Pu} + {}^0_{-1}\beta$                          | 24,400 yr |
| 95            | Americium     | Am     | ${}^{239}_{94}\text{Pu} + {}^1_0\text{n} \longrightarrow {}^{240}_{95}\text{Am} + {}^0_{-1}\beta$         | 51 h      |
| 96            | Curium        | Cm     | ${}^{239}_{94}\text{Pu} + {}^4_2\alpha \longrightarrow {}^{242}_{96}\text{Cm} + {}^1_0\text{n}$           | 163 d     |
| 97            | Berkelium     | Bk     | ${}^{241}_{95}\text{Am} + {}^4_2\alpha \longrightarrow {}^{243}_{97}\text{Bk} + {}^2_1\text{n}$           | 4.6 h     |
| 98            | Californium   | Cf     | ${}^{242}_{96}\text{Cm} + {}^4_2\alpha \longrightarrow {}^{245}_{98}\text{Cf} + {}^1_0\text{n}$           | 44 m      |
| 99            | Einsteinium   | Es     | ${}^{238}_{92}\text{U} + {}^{15}_0\text{n} \longrightarrow {}^{253}_{99}\text{Es} + {}^7_{-1}\beta$       | 20.5 d    |
| 100           | Fermium       | Fm     | ${}^{238}_{92}\text{U} + {}^{17}_0\text{n} \longrightarrow {}^{255}_{100}\text{Fm} + {}^8_{-1}\beta$      | 20.1 h    |
| 101           | Mendelevium   | Md     | ${}^{253}_{99}\text{Es} + {}^4_2\alpha \longrightarrow {}^{256}_{101}\text{Md} + {}^1_0\text{n}$          | 1.5 h     |
| 102           | Nobelium      | No     | ${}^{246}_{96}\text{Cm} + {}^{12}_6\text{C} \longrightarrow {}^{254}_{102}\text{No} + {}^4_0\text{n}$     | 55 s      |
| 103           | Lawrencium    | Lr     | ${}^{252}_{98}\text{Cf} + {}^{10}_5\text{B} \longrightarrow {}^{257}_{103}\text{Lr} + {}^5_0\text{n}$     | 4.2 s     |
| 104           | Rutherfordium | Rf     | ${}^{249}_{98}\text{Cf} + {}^{12}_6\text{C} \longrightarrow {}^{257}_{104}\text{Rf} + {}^4_0\text{n}$     | 4.7 s     |
| 105           | Dubnium       | Db     | ${}^{249}_{98}\text{Cf} + {}^{15}_7\text{N} \longrightarrow {}^{260}_{105}\text{Db} + {}^4_0\text{n}$     | 1.5 s     |
| 106           | Seaborgium    | Sg     | ${}^{249}_{98}\text{Cf} + {}^{18}_8\text{O} \longrightarrow {}^{263}_{106}\text{Sg} + {}^4_0\text{n}$     | 0.8 s     |
| 107           | Bohrium       | Bh     | ${}^{209}_{83}\text{Bi} + {}^{54}_{24}\text{Cr} \longrightarrow {}^{262}_{107}\text{Bh} + {}^1_0\text{n}$ | 17 s      |
| 108           | Hassium       | Hs     | ${}^{208}_{82}\text{Pb} + {}^{58}_{26}\text{Fe} \longrightarrow {}^{265}_{108}\text{Hs} + {}^1_0\text{n}$ | 2.0 ms    |
| 109           | Meitnerium    | Mt     | ${}^{209}_{83}\text{Bi} + {}^{58}_{26}\text{Fe} \longrightarrow {}^{266}_{109}\text{Mt} + {}^1_0\text{n}$ | 3.4 ms    |

## 21.5 Nuclear Fission



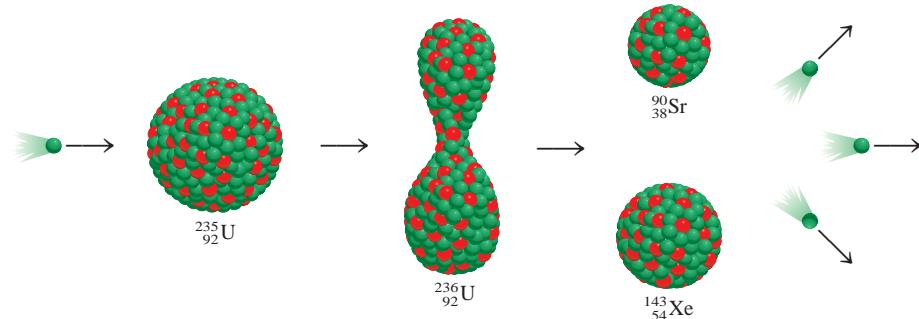
**Animation:**  
Nuclear Fission  
ARIS Animations

**Nuclear fission** is the process in which a heavy nucleus (*mass number > 200*) divides to form smaller nuclei of intermediate mass and one or more neutrons. Because the heavy nucleus is less stable than its products (see Figure 21.2), this process releases a large amount of energy.

The first nuclear fission reaction to be studied was that of uranium-235 bombarded with slow neutrons, whose speed is comparable to that of air molecules at room temperature. Under these conditions, uranium-235 undergoes fission, as shown in Figure 21.6. Actually, this reaction is very complex: More than 30 different elements have been found among the fission products (Figure 21.7). A representative reaction is

**Figure 21.6**

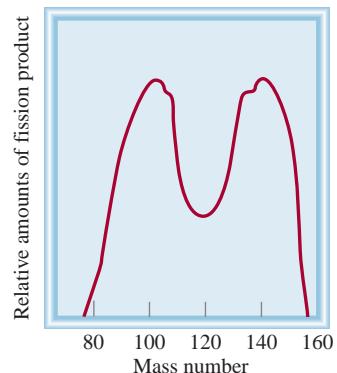
Nuclear fission of  ${}^{235}\text{U}$ . When a  ${}^{235}\text{U}$  nucleus captures a neutron (green dot), it undergoes fission to yield two smaller nuclei. On the average, 2.4 neutrons are emitted for every  ${}^{235}\text{U}$  nucleus that divides.



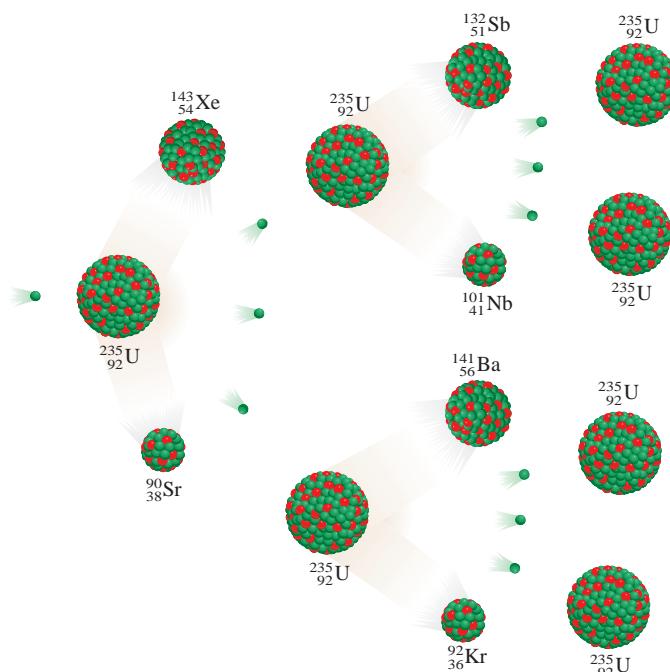
Although many heavy nuclei can be made to undergo fission, only the fission of naturally occurring uranium-235 and of the artificial isotope plutonium-239 has any practical importance. Table 21.5 shows the nuclear binding energies of uranium-235 and its fission products. As the table shows, the binding energy per nucleon for uranium-235 is less than the sum of the binding energies for strontium-90 and xenon-143. Therefore, when a uranium-235 nucleus is split into two smaller nuclei, a certain amount of energy is released. Let us estimate the magnitude of this energy. The difference between the binding energies of the reactants and products is  $(1.23 \times 10^{-10} + 1.92 \times 10^{-10}) \text{ J} - (2.82 \times 10^{-10}) \text{ J}$ , or  $3.3 \times 10^{-11} \text{ J}$  per uranium-235 nucleus. For 1 mole of uranium-235, the energy released would be  $(3.3 \times 10^{-11}) \times (6.02 \times 10^{23})$ , or  $2.0 \times 10^{13} \text{ J}$ . This is an extremely exothermic reaction, considering that the heat of combustion of 1 ton of coal is only about  $5 \times 10^7 \text{ J}$ .

The significant feature of uranium-235 fission is not just the enormous amount of energy released, but the fact that more neutrons are produced than are originally captured in the process. This property makes possible a **nuclear chain reaction**, which is a *self-sustaining sequence of nuclear fission reactions*. The neutrons generated during the initial stages of fission can induce fission in other uranium-235 nuclei, which in turn produce more neutrons, and so on. In less than a second, the reaction can become uncontrollable, liberating a tremendous amount of heat to the surroundings.

Figure 21.8 shows a nuclear chain reaction. For such a chain reaction to occur, enough uranium-235 must be present in the sample to capture the neutrons generated in the fission reaction. Otherwise, many of the neutrons will escape from the sample and the chain reaction will not occur. In this situation, the mass of the sample is said to be *subcritical*. When the amount of the fissionable material is equal to or greater than the **critical mass**, the minimum mass of fissionable material required to generate



**Figure 21.7**  
Relative yields of the products resulting from the fission of U-235, as a function of mass number.



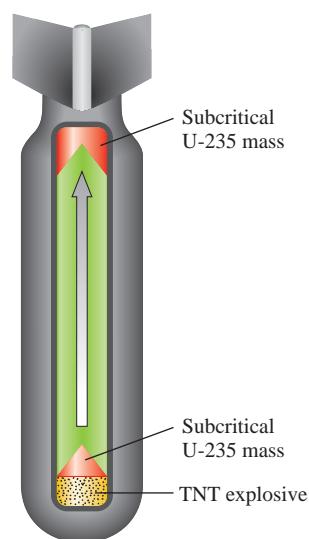
**Figure 21.8**

If a critical mass is present, many of the neutrons emitted during the fission process will be captured by other  $^{235}\text{U}$  nuclei and a chain reaction will occur.

**TABLE 21.5**

**Nuclear Binding Energies of  $^{235}\text{U}$  and Its Fission Products**

|                   | Nuclear Binding Energy           |
|-------------------|----------------------------------|
| $^{235}\text{U}$  | $2.82 \times 10^{-10} \text{ J}$ |
| $^{90}\text{Sr}$  | $1.23 \times 10^{-10} \text{ J}$ |
| $^{143}\text{Xe}$ | $1.92 \times 10^{-10} \text{ J}$ |

**Figure 21.9**

Schematic cross section of an atomic bomb. The TNT explosives are set off first. The explosion forces the sections of fissionable material together to form an amount considerably larger than the critical mass.

a self-sustaining nuclear chain reaction, most of the neutrons will be captured by uranium-235 nuclei, and a chain reaction will occur.

## The Atomic Bomb

The first application of nuclear fission was in the development of the atomic bomb. How is such a bomb made and detonated? The crucial factor in the bomb's design is the determination of the critical mass for the bomb. A small atomic bomb is equivalent to 20,000 tons of TNT (trinitrotoluene). Because 1 ton of TNT releases about  $4 \times 10^9$  J of energy, 20,000 tons would produce  $8 \times 10^{13}$  J. Earlier we saw that 1 mole, or 235 g, of uranium-235 liberates  $2.0 \times 10^{13}$  J of energy when it undergoes fission. Thus, the mass of the isotope present in a small bomb must be at least

$$235 \text{ g} \times \frac{8 \times 10^{13} \text{ J}}{2.0 \times 10^{13} \text{ J}} \approx 1 \text{ kg}$$

For obvious reasons, an atomic bomb is never assembled with the critical mass already present. Instead, the critical mass is formed by using a conventional explosive, such as TNT, to force the fissionable sections together, as shown in Figure 21.9. Neutrons from a source at the center of the device trigger the nuclear chain reaction. Uranium-235 was the fissionable material in the bomb dropped on Hiroshima, Japan, on August 6, 1945. Plutonium-239 was used in the bomb exploded over Nagasaki three days later. The fission reactions generated were similar in these two cases, as was the extent of the destruction.

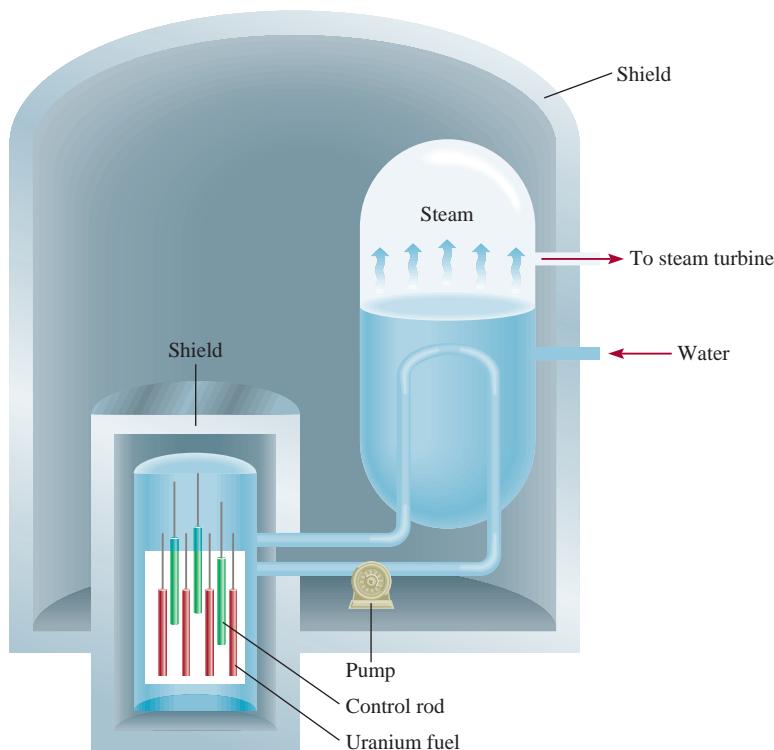
## Nuclear Reactors

A peaceful but controversial application of nuclear fission is the generation of electricity using heat from a controlled chain reaction in a nuclear reactor. Currently, nuclear reactors provide about 20 percent of the electrical energy in the United States. This is a small but by no means negligible contribution to the nation's energy production. Several different types of nuclear reactors are in operation; we will briefly discuss the main features of three of them, along with their advantages and disadvantages.

### Light Water Reactors

Most of the nuclear reactors in the United States are *light water reactors*. Figure 21.10 is a schematic diagram of such a reactor, and Figure 21.11 shows the refueling process in the core of a nuclear reactor.

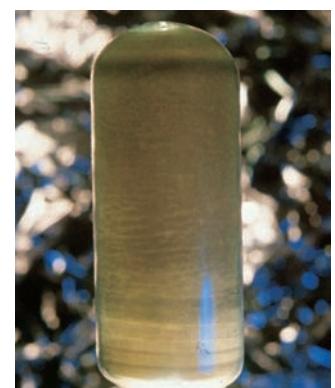
An important aspect of the fission process is the speed of the neutrons. Slow neutrons split uranium-235 nuclei more efficiently than do fast ones. Because fission reactions are highly exothermic, the neutrons produced usually move at high velocities. For greater efficiency, they must be slowed down before they can be used to induce nuclear disintegration. To accomplish this goal, scientists use **moderators**, which are substances that can reduce the kinetic energy of neutrons. A good moderator must satisfy several requirements: It should be nontoxic and inexpensive (as very large quantities of it are necessary); and it should resist conversion into a radioactive substance by neutron bombardment. Furthermore, it is advantageous for the moderator to be a fluid so that it can also be used as a coolant. No substance fulfills all these requirements, although water comes closer than many others that

**Figure 21.10**

Schematic diagram of a nuclear fission reactor. The fission process is controlled by cadmium or boron rods. The heat generated by the process is used to produce steam for the generation of electricity via a heat exchange system.

**Figure 21.11**

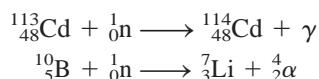
Refueling the core of a nuclear reactor.

**Figure 21.12**

Uranium oxide,  $U_3O_8$ .

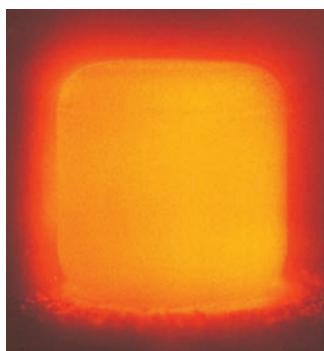
have been considered. Nuclear reactors that use light water ( $H_2O$ ) as a moderator are called light water reactors because  $^1H$  is the lightest isotope of the element hydrogen.

The nuclear fuel consists of uranium, usually in the form of its oxide,  $U_3O_8$  (Figure 21.12). Naturally occurring uranium contains about 0.7 percent of the uranium-235 isotope, which is too low a concentration to sustain a small-scale chain reaction. For effective operation of a light water reactor, uranium-235 must be enriched to a concentration of 3 or 4 percent. In principle, the main difference between an atomic bomb and a nuclear reactor is that the chain reaction that takes place in a nuclear reactor is kept under control at all times. The factor limiting the rate of the reaction is the number of neutrons present. This can be controlled by lowering cadmium or boron control rods between the fuel elements. These rods capture neutrons according to the equations



where  $\gamma$  denotes gamma rays. Without the control rods the reactor core would melt from the heat generated and release radioactive materials into the environment.

Nuclear reactors have rather elaborate cooling systems that absorb the heat given off by the nuclear reaction and transfer it outside the reactor core, where it is used to produce enough steam to drive an electric generator. In this respect, a nuclear power plant is similar to a conventional power plant that burns fossil fuel. In both cases, large quantities of cooling water are needed to condense steam for reuse. Thus, most nuclear power plants are built near a river or a lake. Unfortunately this method of cooling causes thermal pollution (see Section 13.4).



**Figure 21.13**  
The red glow of the radioactive plutonium oxide,  $\text{PuO}_2$ .

### Heavy Water Reactors

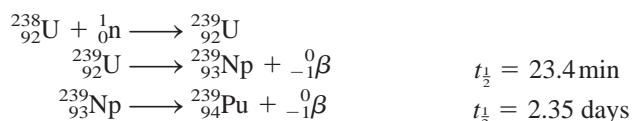
Another type of nuclear reactor uses  $\text{D}_2\text{O}$ , or heavy water, as the moderator, rather than  $\text{H}_2\text{O}$ . Deuterium absorbs neutrons much less efficiently than does ordinary hydrogen. Because fewer neutrons are absorbed, the reactor is more efficient and does not require enriched uranium. The fact that deuterium is a less efficient moderator has a negative impact on the operation of the reactor, because more neutrons leak out of the reactor. However, this is not a serious disadvantage.

The main advantage of a heavy water reactor is that it eliminates the need for building expensive uranium enrichment facilities. However,  $\text{D}_2\text{O}$  must be prepared by either fractional distillation or electrolysis of ordinary water, which can be very expensive considering the amount of water used in a nuclear reactor. In countries where hydroelectric power is abundant, the cost of producing  $\text{D}_2\text{O}$  by electrolysis can be reasonably low. At present, Canada is the only nation successfully using heavy water nuclear reactors. The fact that no enriched uranium is required in a heavy water reactor enables a country to enjoy the benefits of nuclear power without undertaking work that is closely associated with weapons technology.

### Breeder Reactors

A *breeder reactor* uses uranium fuel, but unlike a conventional nuclear reactor, it produces more fissionable materials than it uses.

We know that when uranium-238 is bombarded with fast neutrons, the following reactions take place:



Plutonium-239 forms plutonium oxide, which can be readily separated from uranium.

In this manner the nonfissionable uranium-238 is transmuted into the fissionable isotope plutonium-239 (Figure 21.13).

In a typical breeder reactor, nuclear fuel containing uranium-235 or plutonium-239 is mixed with uranium-238 so that breeding takes place within the core. For every uranium-235 (or plutonium-239) nucleus undergoing fission, more than one neutron is captured by uranium-238 to generate plutonium-239. Thus, the stockpile of fissionable material can be steadily increased as the starting nuclear fuels are consumed. It takes about 7 to 10 yr to regenerate the sizable amount of material needed to refuel the original reactor and to fuel another reactor of comparable size. This interval is called the *doubling time*.

To date, the United States does not have a single operating breeder reactor, and only a few have been built in other countries, such as France and Russia. One problem is economics; breeder reactors are more expensive to build than conventional reactors. There are also more technical difficulties associated with the construction of such reactors. As a result, the future of breeder reactors, in the United States at least, is rather uncertain.

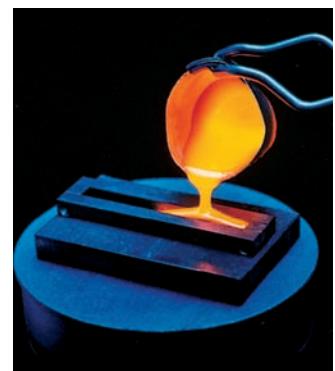
### Hazards of Nuclear Energy

Many people, including environmentalists, regard nuclear fission as a highly undesirable method of energy production. Many fission products such as strontium-90 are dangerous radioactive isotopes with long half-lives. Plutonium-239, used as a nuclear fuel and produced in breeder reactors, is one of the most toxic substances known. It is an alpha emitter with a half-life of 24,400 yr.

Accidents, too, present many dangers. An accident at the Three Mile Island reactor in Pennsylvania in 1979 first brought the potential hazards of nuclear plants to public attention. In this instance, very little radiation escaped the reactor, but the plant remained closed for more than a decade while repairs were made and safety issues addressed. Only a few years later, on April 26, 1986, a reactor at the Chernobyl nuclear plant in Ukraine surged out of control, resulting in a chemical explosion and fire. This accident released much radioactive material into the environment. People working near the plant died within weeks as a result of the exposure to the intense radiation. The long-term effect of the radioactive fallout from this incident has not yet been clearly assessed, although agriculture and dairy farming were affected by the fallout. The number of potential cancer deaths attributable to the radiation contamination is estimated to be between a few thousand and more than 100,000.

In addition to the risk of accidents, the problem of radioactive waste disposal has not been satisfactorily resolved even for safely operated nuclear plants. Many suggestions have been made as to where to store or dispose of nuclear waste, including burial underground, burial beneath the ocean floor, and storage in deep geologic formations. But none of these sites has proved absolutely safe in the long run. Leakage of radioactive wastes into underground water, for example, can endanger nearby communities. The ideal disposal site would seem to be the sun, where a bit more radiation would make little difference, but this kind of operation requires 100 percent reliability in space technology.

Because of the hazards, the future of nuclear reactors is clouded. What was once hailed as the ultimate solution to our energy needs in the twenty-first century is now being debated and questioned by both the scientific community and laypeople. It seems likely that the controversy will continue for some time.



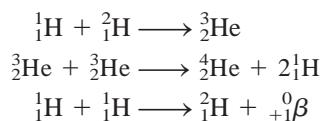
Molten glass is poured over nuclear waste before burial.

## 21.6 Nuclear Fusion

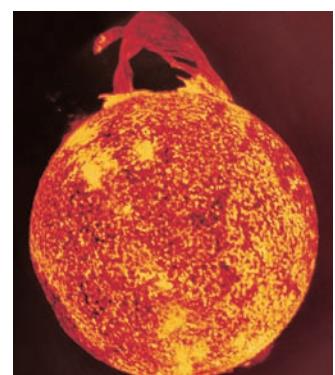
In contrast to the nuclear fission process, **nuclear fusion**, *the combining of small nuclei into larger ones*, is largely exempt from the waste disposal problem.

Figure 21.2 showed that for the lightest elements, nuclear stability increases with increasing mass number. This behavior suggests that if two light nuclei combine or fuse together to form a larger, more stable nucleus, an appreciable amount of energy will be released in the process. This is the basis for ongoing research into the harnessing of nuclear fusion for the production of energy.

Nuclear fusion occurs constantly in the sun. The sun is made up mostly of hydrogen and helium. In its interior, where temperatures reach about 15 million degrees Celsius, the following fusion reactions are believed to take place:



Because *fusion reactions take place only at very high temperatures*, they are often called **thermonuclear reactions**.



Nuclear fusion keeps the temperature in the interior of the sun at about 15 million °C.

## Fusion Reactors

A major concern in choosing the proper nuclear fusion process for energy production is the temperature necessary to carry out the process. Some promising reactions are

| Reaction   | Energy Released                 |
|--|---------------------------------|
| ${}^2\text{H} + {}^2\text{H} \longrightarrow {}^3\text{H} + {}^1\text{H}$  | $6.3 \times 10^{-13} \text{ J}$ |
| ${}^2\text{H} + {}^3\text{H} \longrightarrow {}^4\text{He} + {}^1\text{n}$ | $2.8 \times 10^{-12} \text{ J}$ |
| ${}^6\text{Li} + {}^1\text{H} \longrightarrow 2{}^4\text{He}$              | $3.6 \times 10^{-12} \text{ J}$ |

These reactions take place at extremely high temperatures, on the order of 100 million degrees Celsius, to overcome the repulsive forces between the nuclei. The first reaction is particularly attractive because the world's supply of deuterium is virtually inexhaustible. The total volume of water on Earth is about  $1.5 \times 10^{21} \text{ L}$ . Because the natural abundance of deuterium is  $1.5 \times 10^{-2}$  percent, the total amount of deuterium present is roughly  $4.5 \times 10^{21} \text{ g}$ , or  $5.0 \times 10^{15}$  tons. The cost of preparing deuterium is minimal compared with the value of the energy released by the reaction.

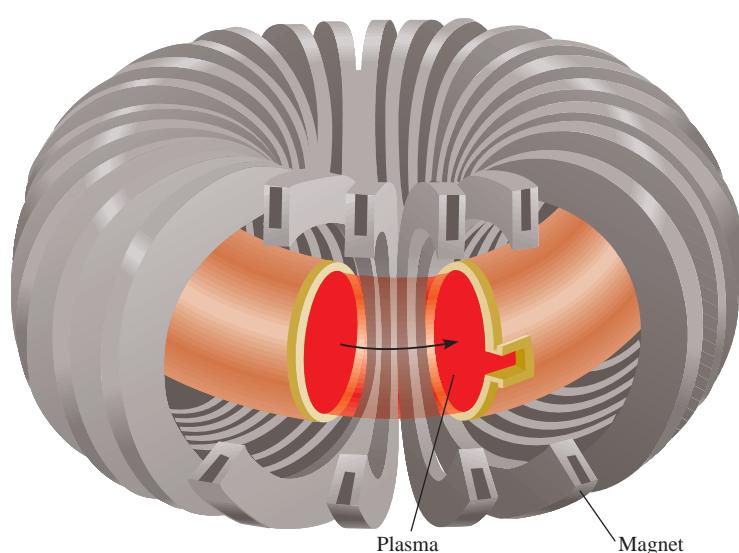
In contrast to the fission process, nuclear fusion looks like a very promising energy source, at least "on paper." Although thermal pollution would be a problem, fusion has the following advantages: (1) The fuels are cheap and almost inexhaustible and (2) the process produces little radioactive waste. If a fusion machine were turned off, it would shut down completely and instantly, without any danger of a meltdown.

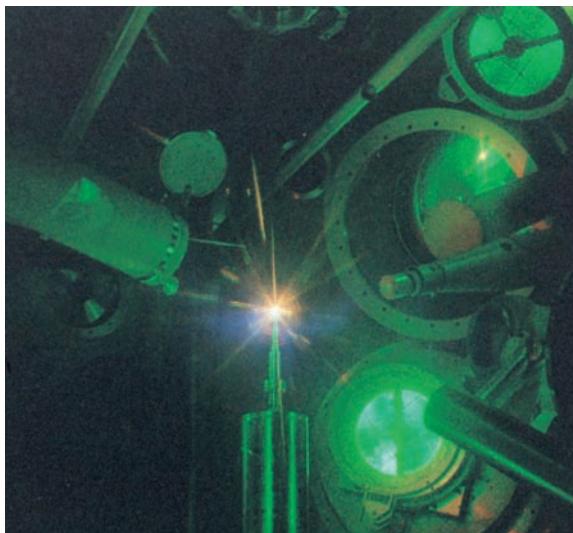
If nuclear fusion is so great, why isn't there even one fusion reactor producing energy? Although we command the scientific knowledge to design such a reactor, the technical difficulties have not yet been solved. The basic problem is finding a way to hold the nuclei together long enough, and at the appropriate temperature, for fusion to occur. At temperatures of about 100 million degrees Celsius, molecules cannot exist, and most or all of the atoms are stripped of their electrons. This *state of matter, a gaseous mixture of positive ions and electrons*, is called **plasma**. The problem of containing this plasma is a formidable one. What solid container can exist at such temperatures? None, unless the amount of plasma is small; but then the solid surface would immediately cool the sample and quench the fusion reaction. One approach to solving this problem is to use *magnetic confinement*. Because a plasma consists of charged particles moving at high speeds, a magnetic field will exert force on it. As Figure 21.14 shows, the plasma moves through a doughnut-shaped tunnel, confined by a complex magnetic field. Thus, the plasma never comes in contact with the walls of the container.

Another promising design employs high-power lasers to initiate the fusion reaction. In test runs, a number of laser beams transfer energy to a small fuel pellet, heating it and causing it to *implode*, that is, to collapse inward from all sides and compress

**Figure 21.14**

A magnetic plasma confinement design called tokamak.



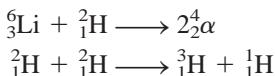
**Figure 21.15**

This small-scale fusion reaction was created at the Lawrence Livermore National Laboratory using a powerful laser, Nova.

into a small volume (Figure 21.15). Consequently, fusion occurs. Like the magnetic confinement approach, laser fusion presents a number of technical difficulties that still need to be overcome before it can be put to practical use on a large scale.

### The Hydrogen Bomb

The technical problems inherent in the design of a nuclear fusion reactor do not affect the production of a hydrogen bomb, also called a thermonuclear bomb. In this case, the objective is all power and no control. Hydrogen bombs do not contain gaseous hydrogen or gaseous deuterium; they contain solid lithium deuteride (LiD), which can be packed very tightly. The detonation of a hydrogen bomb occurs in two stages—first a fission reaction and then a fusion reaction. The required temperature for fusion is achieved with an atomic bomb. Immediately after the atomic bomb explodes, the following fusion reactions occur, releasing vast amounts of energy (Figure 21.16):



There is no critical mass in a fusion bomb, and the force of the explosion is limited only by the quantity of reactants present. Thermonuclear bombs are described as being “cleaner” than atomic bombs because the only radioactive isotopes they produce are tritium, which is a weak  $\beta$ -particle emitter ( $t_{1/2} = 12.5$  yr), and the products of the fission starter. Their damaging effects on the environment can be aggravated, however, by incorporating in the construction some nonfissionable material such as cobalt. Upon bombardment by neutrons, cobalt-59 is converted to cobalt-60, which is a very strong  $\gamma$ -ray emitter with a half-life of 5.2 yr. The presence of radioactive cobalt isotopes in the debris or fallout from a thermonuclear explosion would be fatal to those who survived the initial blast.

**Figure 21.16**

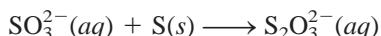
Explosion of a thermonuclear bomb.

## 21.7 Uses of Isotopes

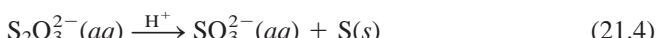
Radioactive and stable isotopes alike have many applications in science and medicine. We have previously described the use of isotopes in dating artifacts (Section 21.3). In this section we will discuss a few more examples.

## Structural Determination

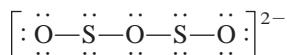
The formula of the thiosulfate ion is  $\text{S}_2\text{O}_3^{2-}$ . For some years chemists were uncertain as to whether the two sulfur atoms occupied equivalent positions in the ion. The thiosulfate ion is prepared by treatment of the sulfite ion with elemental sulfur:



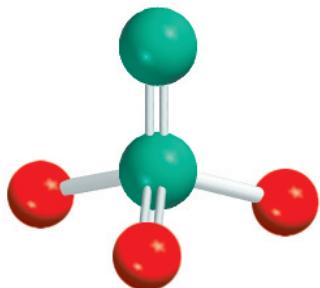
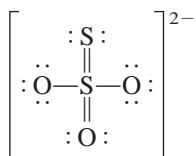
When thiosulfate is treated with dilute acid, the reaction is reversed. The sulfite ion is reformed and elemental sulfur precipitates:



If this sequence is started with elemental sulfur enriched with the radioactive sulfur-35 isotope, the isotope acts as a “label” for S atoms. All the labels are found in the sulfur precipitate in Equation (21.4); none of them appears in the final sulfite ions. Clearly, then, the two atoms of sulfur in  $\text{S}_2\text{O}_3^{2-}$  are not structurally equivalent, as would be the case if the structure were



Otherwise, the radioactive isotope would be present in both the elemental sulfur precipitate and the sulfite ion. Based on spectroscopic studies, we now know that the structure of the thiosulfate ion is



## Study of Photosynthesis

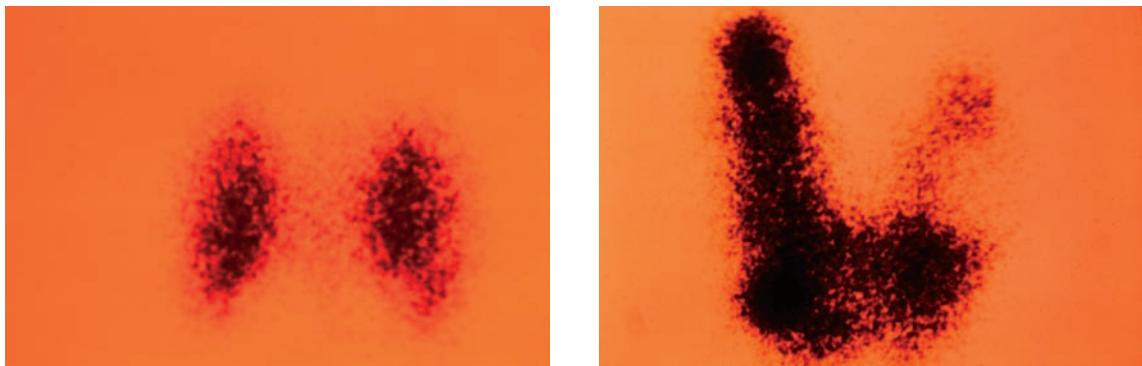
The study of photosynthesis is also rich with isotope applications. The overall photosynthesis reaction can be represented as



The radioactive  $^{14}\text{C}$  isotope has helped to determine the path of carbon in photosynthesis. Starting with  $^{14}\text{CO}_2$ , it was possible to isolate the intermediate products during photosynthesis and measure the amount of radioactivity of each carbon-containing compound. In this manner, the path from  $\text{CO}_2$  through various intermediate compounds to carbohydrate could be clearly charted. *Isotopes, especially radioactive isotopes that are used to trace the path of the atoms of an element in a chemical or biological process, are called tracers.*

## Isotopes in Medicine

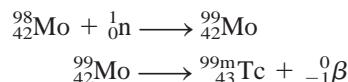
Tracers are used also for diagnosis in medicine. Sodium-24 (a  $\beta$  emitter with a half-life of 14.8 h) injected into the bloodstream as a salt solution can be monitored to trace the flow of blood and detect possible constrictions or obstructions in the circulatory system. Iodine-131 (a  $\beta$  emitter with a half-life of 8 days) has been used to test the activity of the thyroid gland. A malfunctioning thyroid can be detected by giving the patient a drink of a solution containing a known amount of  $\text{Na}^{131}\text{I}$  and measuring the radioactivity just above the thyroid to see if the iodine is absorbed at the normal rate. Of course, the amounts of

**Figure 21.17**

After ingesting  $\text{Na}^{131}\text{I}$ , the uptake of the radioactive iodine by the thyroid gland in a patient is monitored with a scanner. The photos show a normal thyroid gland (left) and an enlarged thyroid gland (right).

radioisotope used in the human body must always be kept small; otherwise, the patient might suffer permanent damage from the high-energy radiation. Another radioactive isotope of iodine, iodine-123 (a  $\gamma$ -ray emitter), is used to image the thyroid gland (Figure 21.17).

Technetium, the first artificially prepared element, is one of the most useful elements in nuclear medicine. Although technetium is a transition metal, all its isotopes are radioactive. In the laboratory, it is prepared by the nuclear reactions



where the superscript m denotes that the technetium-99 isotope is produced in its excited nuclear state. This isotope has a half-life of about 6 hours, decaying by  $\gamma$  radiation to technetium-99 in its nuclear ground state. Thus, it is a valuable diagnostic tool. The patient either drinks or is injected with a solution containing  ${}^{99\text{m}}\text{Tc}$ . By detecting the  $\gamma$  rays emitted by  ${}^{99\text{m}}\text{Tc}$ , doctors can obtain images of organs such as the heart, liver, and lungs.

A major advantage of using radioactive isotopes as tracers is that they are easy to detect. Their presence even in very small amounts can be detected by photographic techniques or by devices known as counters. Figure 21.18 is a diagram of a Geiger counter, an instrument widely used in scientific work and medical laboratories to detect radiation.

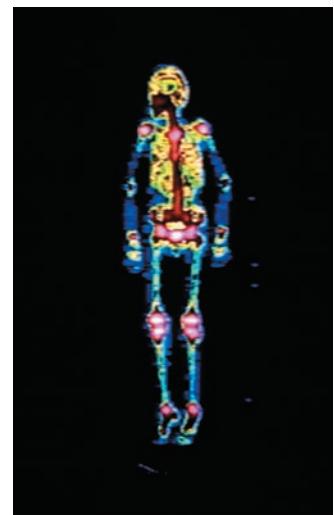
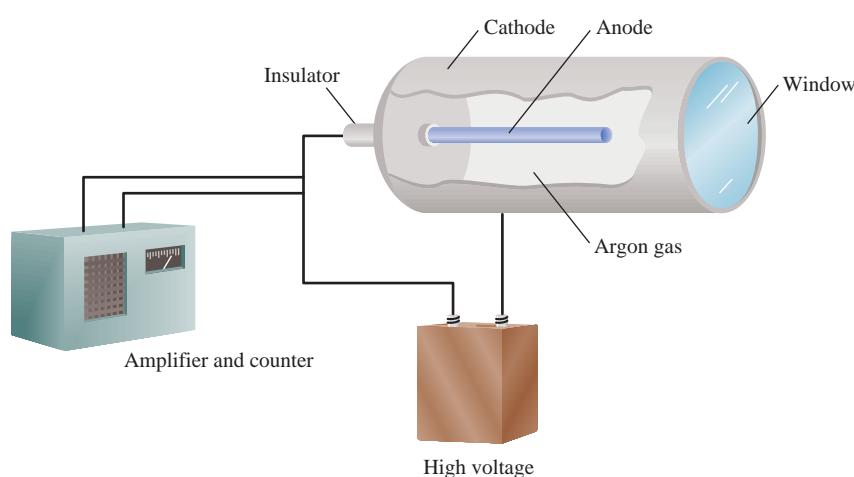


Image of a person's skeleton obtained using  ${}^{99\text{m}}_{43}\text{Tc}$ .

**Figure 21.18**

Schematic diagram of a Geiger counter. Radiation ( $\alpha$ ,  $\beta$ , or  $\gamma$  rays) entering through the window ionized the argon gas to generate a small current flow between the electrodes. This current is amplified and is used to flash a light or operate a counter with a clicking sound.

## 21.8 Biological Effects of Radiation

In this section we will examine briefly the effects of radiation on biological systems. But first let us define quantitative measures of radiation. The fundamental unit of radioactivity is the *curie* (Ci); 1 Ci corresponds to exactly  $3.70 \times 10^{10}$  nuclear disintegrations per second. This decay rate is equivalent to that of 1 g of radium. A *millicurie* (mCi) is one-thousandth of a curie. Thus, 10 mCi of a carbon-14 sample is the quantity that undergoes

$$(10 \times 10^{-3})(3.70 \times 10^{10}) = 3.70 \times 10^8$$

disintegrations per second.

The intensity of radiation depends on the number of disintegrations as well as on the energy and type of radiation emitted. One common unit for the absorbed dose of radiation is the *rad* (*radiation absorbed dose*), which is the amount of radiation that results in the absorption of  $1 \times 10^{-2}$  J per kilogram of irradiated material. The biological effect of radiation also depends on the part of the body irradiated and the type of radiation. For this reason, the rad is often multiplied by a factor called *RBE* (*relative biological effectiveness*). The RBE is approximately 1 for beta and gamma radiation and about 10 for alpha radiation. To measure the biological damage, which depends on dose rate, total dose, and the type of tissue affected, we introduce another term called a *rem* (*roentgen equivalent for man*), given by

$$\text{number of rems} = (\text{number of rads})(\text{RBE}) \quad (21.5)$$

Of the three types of nuclear radiation, alpha particles usually have the least penetrating power. Beta particles are more penetrating than alpha particles, but less so than gamma rays. Gamma rays have very short wavelengths and high energies. Furthermore, because they carry no charge, they cannot be stopped by shielding materials as easily as alpha and beta particles. However, if alpha or beta emitters are ingested, their damaging effects are greatly aggravated because the organs will be constantly subject to damaging radiation at close range. For example, strontium-90, a beta emitter, can replace calcium in bones, where it does the greatest damage.

Table 21.6 lists the average amounts of radiation an American receives every year. It should be pointed out that for short-term exposures to radiation, a dosage of 50–200 rem will cause a decrease in white blood cell counts and other complications, while

**TABLE 21.6** Average Yearly Radiation Doses for Americans

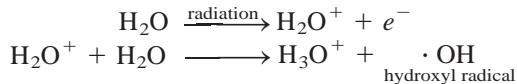
| Source                     | Dose (mrem/yr)* |
|----------------------------|-----------------|
| Cosmic rays                | 20–50           |
| Ground and surroundings    | 25              |
| Human body <sup>†</sup>    | 26              |
| Medical and dental X rays  | 50–75           |
| Air travel                 | 5               |
| Fallout from weapons tests | 5               |
| Nuclear waste              | 2               |
| Total                      | 133–188         |

\*1 mrem = 1 millirem =  $1 \times 10^{-3}$  rem.

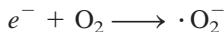
<sup>†</sup>The radioactivity in the body comes from food and air.

a dosage of 500 rem or greater may result in death within weeks. Current safety standards permit nuclear workers to be exposed to no more than 5 rem per year and specify a maximum of 0.5 rem of human-made radiation per year for the general public.

The chemical basis of radiation damage is that of ionizing radiation. Radiation of either particles or gamma rays can remove electrons from atoms and molecules in its path, leading to the formation of ions and radicals. Radicals are usually short-lived and highly reactive. For example, when water is irradiated with gamma rays, the following reactions take place:



The electron (in the hydrated form) can subsequently react with water or with a hydrogen ion to form atomic hydrogen, and with oxygen to produce the superoxide ion,  $\text{O}_2^-$  (a radical):



In the tissues the superoxide ions and other free radicals attack cell membranes and a host of organic compounds, such as enzymes and DNA molecules. Organic compounds can themselves be directly ionized and destroyed by high-energy radiation.

It has long been known that exposure to high-energy radiation can induce cancer in humans and other animals. Cancer is characterized by uncontrolled cellular growth. On the other hand, it is also well established that cancer cells can be destroyed by proper radiation treatment. In radiation therapy, a compromise is sought. The radiation to which the patient is exposed must be sufficient to destroy cancer cells without killing too many normal cells and, it is hoped, without inducing another form of cancer.

Radiation damage to living systems is generally classified as *somatic* or *genetic*. Somatic injuries are those that affect the organism during its own lifetime. Sunburn, skin rash, cancer, and cataracts are examples of somatic damage. Genetic damage means inheritable changes or gene mutations. For example, a person whose chromosomes have been damaged or altered by radiation may have deformed offspring.

**Chromosomes are parts of the cell structure that contain the genetic material (DNA).**

## KEY EQUATIONS

$$E = mc^2 \quad (21.1) \quad \text{Einstein's mass-energy equivalence relationship.}$$

$$\Delta E = (\Delta m)c^2 \quad (21.2) \quad \text{Relation between mass defect and energy released.}$$

$$\text{nuclear binding energy per nucleon} = \frac{\text{nuclear binding energy}}{\text{number of nucleons}} \quad (21.3)$$

## SUMMARY OF FACTS AND CONCEPTS

1. Nuclear chemistry is the study of changes in atomic nuclei. Such changes are termed nuclear reactions. Radioactive decay and nuclear transmutation are nuclear reactions.
2. For stable nuclei of low atomic number, the neutron-to-proton ratio is close to 1. For heavier stable nuclei, the

ratio becomes greater than 1. All nuclei with 84 or more protons are unstable and radioactive. Nuclei with even atomic numbers are more stable than those with odd atomic numbers. A quantitative measure of nuclear stability is the nuclear binding energy, which can be calculated from a knowledge of the mass defect of the nucleus.

- Radioactive nuclei emit  $\alpha$  particles,  $\beta$  particles, positrons, or  $\gamma$  rays. The equation for a nuclear reaction includes the particles emitted, and both the mass numbers and the atomic numbers must balance. Uranium-238 is the parent of a natural radioactive decay series. A number of radioactive isotopes, such as  $^{238}\text{U}$  and  $^{14}\text{C}$ , can be used to date objects. Artificially radioactive elements are created by the bombardment of other elements by accelerated neutrons, protons, or  $\alpha$  particles.
- Nuclear fission is the splitting of a large nucleus into smaller nuclei plus neutrons. When these neutrons are captured efficiently by other nuclei, an uncontrollable chain reaction can occur. Nuclear reactors use the heat
- from a controlled nuclear fission reaction to produce power. The three important types of reactors are light water reactors, heavy water reactors, and breeder reactors.
- Nuclear fusion, the type of reaction that occurs in the sun, is the combination of two light nuclei to form one heavy nucleus. Fusion takes place only at very high temperatures—so high that controlled large-scale nuclear fusion has so far not been achieved.
- Radioactive isotopes are easy to detect and thus make excellent tracers in chemical reactions and in medical practice. High-energy radiation damages living systems by causing ionization and the formation of reactive radicals.

## KEY WORDS

Breeder reactor, p. 726  
 Critical mass, p. 723  
 Mass defect, p. 713  
 Moderators, p. 724  
 Nuclear binding energy, p. 713

Nuclear chain reaction, p. 723  
 Nuclear fission, p. 722  
 Nuclear fusion, p. 727  
 Nuclear reaction, p. 709  
 Nuclear transmutation, p. 709

Plasma, p. 728  
 Positron, p. 710  
 Radioactive decay series,  
 p. 716  
 Thermonuclear reaction, p. 727

Tracer, p. 730  
 Transuranium elements,  
 p. 721

## QUESTIONS AND PROBLEMS

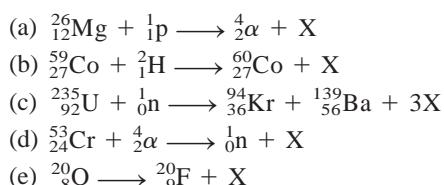
### Nuclear Reactions

#### Review Questions

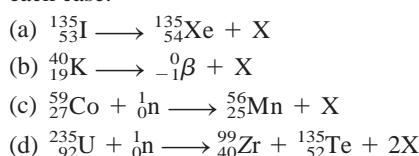
- How do nuclear reactions differ from ordinary chemical reactions?
- What are the steps in balancing nuclear equations?
- What is the difference between  $-_1^0e$  and  $-_1^0\beta$ ?
- What is the difference between an electron and a positron?

#### Problems

- Complete these nuclear equations and identify X in each case:



- Complete these nuclear equations and identify X in each case:



### Nuclear Stability

#### Review Questions

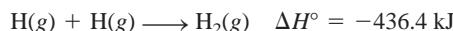
- State the general rules for predicting nuclear stability.
- What is the belt of stability?
- Why is it impossible for the isotope  $^2_2\text{He}$  to exist?
- Define nuclear binding energy, mass defect, and nucleon.
- How does Einstein's equation,  $E = mc^2$ , enable us to calculate nuclear binding energy?
- Why is it preferable to use nuclear binding energy per nucleon for a comparison of the stabilities of different nuclei?

#### Problems

- The radius of a uranium-235 nucleus is about  $7.0 \times 10^{-3}$  pm. Calculate the density of the nucleus in  $\text{g/cm}^3$ . (Assume the atomic mass is 235 amu.)
- For each pair of isotopes listed, predict which one is less stable: (a)  $^6_3\text{Li}$  or  $^9_3\text{Li}$ , (b)  $^{23}_{11}\text{Na}$  or  $^{25}_{11}\text{Na}$ , (c)  $^{48}_{20}\text{Ca}$  or  $^{48}_{21}\text{Sc}$ .
- For each pair of elements listed, predict which one has more stable isotopes: (a) Co or Ni, (b) F or Se, (c) Ag or Cd.
- In each pair of isotopes shown, indicate which one you would expect to be radioactive: (a)  $^{20}_{10}\text{Ne}$  and

(b)  $^{40}_{10}\text{Ca}$  and  $^{45}_{20}\text{Ca}$ , (c)  $^{95}_{42}\text{Mo}$  and  $^{92}_{43}\text{Tc}$ , (d)  $^{195}_{80}\text{Hg}$  and  $^{196}_{80}\text{Hg}$ , (e)  $^{209}_{83}\text{Bi}$  and  $^{242}_{96}\text{Cm}$ .

- 21.17 Given that



calculate the change in mass (in kg) per mole of  $\text{H}_2$  formed.

- 21.18** Estimates show that the total energy output of the sun is  $5 \times 10^{26} \text{ J/s}$ . What is the corresponding mass loss in kg/s of the sun?
- 21.19 Calculate the nuclear binding energy (in J) and the nuclear binding energy per nucleon of the following isotopes: (a)  $^7_3\text{Li}$  (7.01600 amu) and (b)  $^{35}_{17}\text{Cl}$  (34.95952 amu).
- 21.20** Calculate the nuclear binding energy (in J) and the nuclear binding energy per nucleon of the following isotopes: (a)  $^4_2\text{He}$  (4.0026 amu) and (b)  $^{184}_{74}\text{W}$  (183.9510 amu).

## Natural Radioactivity

### Review Questions

- 21.21 Discuss factors that lead to nuclear decay.
- 21.22 Outline the principle for dating materials using radioactive isotopes.

### Problems

- 21.23 Fill in the blanks in these radioactive decay series:  
 (a)  $^{232}\text{Th} \xrightarrow{\alpha} \underline{\hspace{2cm}} \xrightarrow{\beta} \underline{\hspace{2cm}} \xrightarrow{\beta} \underline{\hspace{2cm}} \xrightarrow{\alpha} \underline{\hspace{2cm}} \xrightarrow{\beta} \underline{\hspace{2cm}}$   
 (b)  $^{235}\text{U} \xrightarrow{\alpha} \underline{\hspace{2cm}} \xrightarrow{\beta} \underline{\hspace{2cm}} \xrightarrow{\alpha} \underline{\hspace{2cm}} \xrightarrow{\alpha} \underline{\hspace{2cm}} \xrightarrow{\alpha} \underline{\hspace{2cm}}$   
 (c)  $\underline{\hspace{2cm}} \xrightarrow{\alpha} \underline{\hspace{2cm}} \xrightarrow{\beta} \underline{\hspace{2cm}} \xrightarrow{\alpha} \underline{\hspace{2cm}}$

- 21.24** A radioactive substance undergoes decay as:

| Time (days) | Mass (g) |
|-------------|----------|
| 0           | 500      |
| 1           | 389      |
| 2           | 303      |
| 3           | 236      |
| 4           | 184      |
| 5           | 143      |
| 6           | 112      |

Calculate the first-order decay constant and the half-life of the reaction.

- 21.25 The radioactive decay of Tl-206 to Pb-206 has a half-life of 4.20 min. Starting with  $5.00 \times 10^{22}$  atoms of Tl-206, calculate the number of such atoms left after 42.0 min.
- 21.26** A freshly isolated sample of  $^{90}\text{Y}$  was found to have an activity of  $9.8 \times 10^5$  disintegrations per minute at 1:00 P.M. on December 3, 2000. At 2:15 P.M. on December 17, 2000, its activity was redetermined

and found to be  $2.6 \times 10^4$  disintegrations per minute. Calculate the half-life of  $^{90}\text{Y}$ .

- 21.27 Why do radioactive decay series obey first-order kinetics?
- 21.28** In the thorium decay series, thorium-232 loses a total of 6  $\alpha$  particles and 4  $\beta$  particles in a 10-stage process. What is the final isotope produced?
- 21.29 Strontium-90 is one of the products of the fission of uranium-235. This strontium isotope is radioactive, with a half-life of 28.1 yr. Calculate how long (in yr) it will take for 1.00 g of the isotope to be reduced to 0.200 g by decay.
- 21.30** Consider the decay series



where A, B, and C are radioactive isotopes with half-lives of 4.50 s, 15.0 days, and 1.00 s, respectively, and D is nonradioactive. Starting with 1.00 mole of A, and none of B, C, or D, calculate the number of moles of A, B, C, and D left after 30 days.

## Nuclear Transmutation

### Review Questions

- 21.31 What is the difference between radioactive decay and nuclear transmutation?
- 21.32 How is nuclear transmutation achieved in practice?

### Problems

- 21.33 Write balanced nuclear equations for these reactions and identify X: (a)  $X(p, \alpha)^{12}_6\text{C}$ , (b)  $^{27}_{13}\text{Al}(d, \alpha)X$ , (c)  $^{55}_{25}\text{Mn}(n, \gamma)X$ .
- 21.34** Write balanced nuclear equations for these reactions and identify X: (a)  $^{80}_{34}\text{Se}(d, p)X$ , (b)  $X(d, 2p)^9_3\text{Li}$ , (c)  $^{10}_5\text{B}(n, \alpha)X$ .
- 21.35 Describe how you would prepare astatine-211, starting with bismuth-209.
- 21.36** A long-cherished dream of alchemists was to produce gold from cheaper and more abundant elements. This dream was finally realized when  $^{198}_{80}\text{Hg}$  was converted into gold by neutron bombardment. Write a balanced equation for this reaction.

## Nuclear Fission

### Review Questions

- 21.37 Define nuclear fission, nuclear chain reaction, and critical mass.
- 21.38 Which isotopes can undergo nuclear fission?
- 21.39 Explain how an atomic bomb works.
- 21.40 Explain the functions of a moderator and a control rod in a nuclear reactor.

- 21.41 Discuss the differences between a light water and a heavy water nuclear fission reactor. What are the advantages of a breeder reactor over a conventional nuclear fission reactor?
- 21.42 What makes water particularly suitable for use as moderator in a nuclear reactor?

## Nuclear Fusion

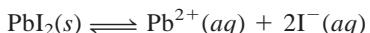
### Review Questions

- 21.43 Define nuclear fusion, thermonuclear reaction, and plasma.
- 21.44 Why do heavy elements such as uranium undergo fission while light elements such as hydrogen and lithium undergo fusion?
- 21.45 How does a hydrogen bomb work?
- 21.46 What are the advantages of a fusion reactor over a fission reactor? What are the practical difficulties in operating a large-scale fusion reactor?

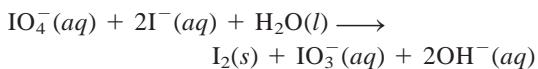
## Uses of Isotopes

### Problems

- 21.47 Describe how you would use a radioactive iodine isotope to demonstrate that the following process is in dynamic equilibrium:



- 21.48** Consider this redox reaction:



When  $\text{KIO}_4$  is added to a solution containing iodide ions labeled with radioactive iodine-128, all the radioactivity appears in  $\text{I}_2$  and none in the  $\text{IO}_3^-$  ion. What can you deduce about the mechanism for the redox process?

- 21.49 Explain how you might use a radioactive tracer to show that ions are not completely motionless in crystals.

- 21.50** Each molecule of hemoglobin, the oxygen carrier in blood, contains four Fe atoms. Explain how you would use the radioactive  ${}_{26}^{59}\text{Fe}$  ( $t_{1/2} = 46$  days) to show that the iron in a certain food is converted into hemoglobin.

## Additional Problems

- 21.51 How does a Geiger counter work?
- 21.52** Nuclei with an even number of protons and an even number of neutrons are more stable than those with an odd number of protons and/or an odd number of neutrons. What is the significance of the even numbers of protons and neutrons in this case?

- 21.53 Tritium,  ${}^3\text{H}$ , is radioactive and decays by electron emission. Its half-life is 12.5 yr. In ordinary water the ratio of  ${}^1\text{H}$  to  ${}^3\text{H}$  atoms is  $1.0 \times 10^{17}$  to 1. (a) Write a balanced nuclear equation for tritium decay. (b) How many disintegrations will be observed per minute in a 1.00-kg sample of water?

- 21.54** (a) What is the activity, in millicuries, of a 0.500-g sample of  ${}_{93}^{237}\text{Np}$ ? (This isotope decays by  $\alpha$ -particle emission and has a half-life of  $2.20 \times 10^6$  yr.) (b) Write a balanced nuclear equation for the decay of  ${}_{93}^{237}\text{Np}$ .

- 21.55 These equations are for nuclear reactions that are known to occur in the explosion of an atomic bomb. Identify X.

- (a)  ${}_{92}^{235}\text{U} + {}_0^1\text{n} \longrightarrow {}_{56}^{140}\text{Ba} + {}_0^1\text{n} + \text{X}$   
 (b)  ${}_{92}^{235}\text{U} + {}_0^1\text{n} \longrightarrow {}_{55}^{144}\text{Cs} + {}_{37}^{90}\text{Rb} + 2\text{X}$   
 (c)  ${}_{92}^{235}\text{U} + {}_0^1\text{n} \longrightarrow {}_{35}^{87}\text{Br} + {}_0^1\text{n} + \text{X}$   
 (d)  ${}_{92}^{235}\text{U} + {}_0^1\text{n} \longrightarrow {}_{62}^{160}\text{Sm} + {}_{30}^{72}\text{Zn} + 4\text{X}$

- 21.56** Calculate the nuclear binding energies, in J/nucleon, for these species: (a)  ${}^{10}\text{B}$  (10.0129 amu), (b)  ${}^{11}\text{B}$  (11.00931 amu), (c)  ${}^{14}\text{N}$  (14.00307 amu), (d)  ${}^{56}\text{Fe}$  (55.9349 amu).

- 21.57 Write complete nuclear equations for these processes: (a) tritium,  ${}^3\text{H}$ , undergoes  $\beta$  decay; (b)  ${}^{242}\text{Pu}$  undergoes  $\alpha$ -particle emission; (c)  ${}^{131}\text{I}$  undergoes  $\beta$  decay; (d)  ${}^{251}\text{Cf}$  emits an  $\alpha$  particle.

- 21.58** The nucleus of nitrogen-18 lies above the stability belt. Write an equation for a nuclear reaction by which nitrogen-18 can achieve stability.

- 21.59 Why is strontium-90 a particularly dangerous isotope for humans?

- 21.60** How are scientists able to tell the age of a fossil?

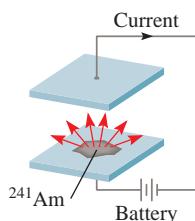
- 21.61 After the Chernobyl accident, people living close to the nuclear reactor site were urged to take large amounts of potassium iodide as a safety precaution. What is the chemical basis for this action?

- 21.62** Astatine, the last member of Group 7A, can be prepared by bombarding bismuth-209 with  $\alpha$  particles. (a) Write an equation for the reaction. (b) Represent the equation in the abbreviated form, as discussed in Section 21.4.

- 21.63 To detect bombs that may be smuggled onto airplanes, the Federal Aviation Administration (FAA) will soon require all major airports in the United States to install thermal neutron analyzers. The thermal neutron analyzer will bombard baggage with low-energy neutrons, converting some of the nitrogen-14 nuclei to nitrogen-15, with simultaneous emission of  $\gamma$  rays. Because nitrogen content is usually high in explosives, detection of a high dosage of  $\gamma$  rays will suggest that a bomb may be present. (a) Write an equation for the nuclear process. (b) Compare this technique with the conventional X-ray detection method.

- 21.64** Explain why achievement of nuclear fusion in the laboratory requires a temperature of about 100 million degrees Celsius, which is much higher than that in the interior of the sun (15 million degrees Celsius).
- 21.65** Tritium contains one proton and two neutrons. There is no proton-proton repulsion present in the nucleus. Why, then, is tritium radioactive?
- 21.66** The carbon-14 decay rate of a sample obtained from a young tree is 0.260 disintegration per second per gram of the sample. Another wood sample prepared from an object recovered at an archaeological excavation gives a decay rate of 0.186 disintegration per second per gram of the sample. What is the age of the object?
- 21.67** The usefulness of radiocarbon dating is limited to objects no older than 50,000 years. What percent of the carbon-14, originally present in the sample, remains after this period of time?
- 21.68** The radioactive potassium-40 isotope decays to argon-40 with a half-life of  $1.2 \times 10^9$  yr. (a) Write a balanced equation for the reaction. (b) A sample of moon rock is found to contain 18 percent potassium-40 and 82 percent argon by mass. Calculate the age of the rock in years.
- 21.69** Both barium (Ba) and radium (Ra) are members of Group 2A and are expected to exhibit similar chemical properties. However, Ra is not found in barium ores. Instead, it is found in uranium ores. Explain.
- 21.70** Nuclear waste disposal is one of the major concerns of the nuclear industry. In choosing a safe and stable environment to store nuclear wastes, consideration must be given to the heat released during nuclear decay. As an example, consider the  $\beta$  decay of  $^{90}\text{Sr}$  (89.907738 amu):
- $$^{90}_{38}\text{Sr} \longrightarrow ^{90}_{39}\text{Y} + {}_{-1}^0\beta \quad t_{\frac{1}{2}} = 28.1 \text{ yr}$$
- The  $^{90}\text{Y}$  (89.907152 amu) further decays as follows:
- $$^{90}_{39}\text{Y} \longrightarrow ^{90}_{40}\text{Zr} + {}_{-1}^0\beta \quad t_{\frac{1}{2}} = 64 \text{ h}$$
- Zirconium-90 (89.904703 amu) is a stable isotope.
- (a) Use the mass defect to calculate the energy released (in joules) in each of the preceding two decays. (The mass of the electron is  $5.4857 \times 10^{-4}$  amu.) (b) Starting with 1 mole of  $^{90}\text{Sr}$ , calculate the number of moles of  $^{90}\text{Sr}$  that will decay in a year. (c) Calculate the amount of heat released (in kilojoules) corresponding to the number of moles of  $^{90}\text{Sr}$  decayed to  $^{90}\text{Zr}$  in (b).
- 21.71** Which of the following poses a greater health hazard: a radioactive isotope with a short half-life or a radioactive isotope with a long half-life? Explain. [Assume same type of radiation ( $\alpha$  or  $\beta$ ) and comparable energetics per particle emitted.]
- 21.72** As a result of being exposed to the radiation released during the Chernobyl nuclear accident, the dose of iodine-131 in a person's body is 7.4 mC (1 mC =  $1 \times 10^{-3}$  Ci). Use the relationship  $\text{rate} = \lambda N$  to calculate the number of atoms of iodine-131 to which this radioactivity corresponds. (The half-life of  $^{131}\text{I}$  is 8.1 days.)
- 21.73** Bismuth-214 is an  $\alpha$ -emitter with a half-life of 19.7 min. A 5.26-mg sample of the isotope is placed in a sealed, evacuated flask of volume 20.0 mL at 40°C. Assuming that all the  $\alpha$  particles generated are converted to helium gas and that the other decay product is nonradioactive, calculate the pressure (in mmHg) inside the flask after 78.8 min. Use 214 amu for the atomic mass of bismuth.
- 21.74** From the definition of curie, calculate Avogadro's number, given that the molar mass of  $^{226}\text{Ra}$  is 226.03 g/mol and that it decays with a half-life of  $1.6 \times 10^3$  yr.
- 21.75** Since 1994, elements 110, 111, 112, and 114 have been synthesized. Element 110 was created by bombarding  $^{208}\text{Pb}$  with  $^{62}\text{Ni}$ ; element 111 was created by bombarding  $^{209}\text{Bi}$  with  $^{64}\text{Ni}$ ; element 112 was created by bombarding  $^{208}\text{Pb}$  with  $^{66}\text{Zn}$ ; element 114 was created by bombarding  $^{244}\text{Pu}$  with  $^{48}\text{Ca}$ . Write an equation for each synthesis. Predict the chemical properties of these elements. Use W for element 110, X for element 111, Y for element 112, and Z for element 114.
- 21.76** Sources of energy on Earth include fossil fuels, geothermal, gravitational, hydroelectric, nuclear fission, nuclear fusion, solar, and wind. Which of these have a "nuclear origin," either directly or indirectly?
- 21.77** A person received an anonymous gift of a decorative box which he placed on his desk. A few months later he became ill and died shortly afterward. After investigation, the cause of his death was linked to the box. The box was air-tight and had no toxic chemicals on it. What might have killed the man?
- 21.78** Identify two of the most abundant radioactive elements that exist on Earth. Explain why they are still present. (You may need to consult a handbook of chemistry.)
- 21.79** (a) Calculate the energy released when a  $^{238}\text{U}$  isotope decays to  $^{234}\text{Th}$ . The atomic masses are given by:  $^{238}\text{U}$ : 238.0508 amu;  $^{234}\text{Th}$ : 234.0436 amu;  $^{4}\text{He}$ : 4.0026 amu. (b) The energy released in (a) is transformed into the kinetic energy of the recoiling  $^{234}\text{Th}$  nucleus and the  $\alpha$  particle. Which of the two will move away faster? Explain.
- 21.80** Cobalt-60 is an isotope used in diagnostic medicine and cancer treatment. It decays with  $\gamma$  ray emission. Calculate the wavelength of the radiation in nanometers if the energy of the  $\gamma$  ray is  $2.4 \times 10^{-13}$  J/photon.
- 21.81** Americium-241 is used in smoke detectors because it has a long half-life (458 yr) and its emitted  $\alpha$  particles are energetic enough to ionize air molecules.

Given the schematic diagram of a smoke detector below, explain how it works.

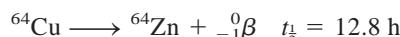


- 21.82** The constituents of wine contain, among others, carbon, hydrogen, and oxygen atoms. A bottle of wine was sealed about 6 yr ago. To confirm its age, which of the isotopes would you choose in a radioactive dating study? The half-lives of the isotopes are:  $^{14}\text{C}$ : 5730 yr;  $^{15}\text{O}$ : 124 s;  $^3\text{H}$ : 12.5 yr. Assume that the activities of the isotopes were known at the time the bottle was sealed.

- 21.83** Name two advantages of a nuclear-powered submarine over a conventional submarine.

- 21.84** In 1997 a scientist at a nuclear research center in Russia placed a thin shell of copper on a sphere of highly enriched uranium-235. Suddenly, there was a huge burst of radiation, which turned the air blue. Three days later, the scientist died of radiation damage. Explain what caused the accident. (*Hint:* Copper is an effective metal for reflecting neutrons.)

- 21.85** A radioactive isotope of copper decays as follows:



Starting with 84.0 g of  $^{64}\text{Cu}$ , calculate the quantity of  $^{64}\text{Zn}$  produced after 18.4 h.

- 21.86** A 0.0100-g sample of a radioactive isotope with a half-life of  $1.3 \times 10^9$  yr decays at the rate of  $2.9 \times 10^4$  dpm. Calculate the molar mass of the isotope.

## SPECIAL PROBLEMS

- 21.87** Describe, with appropriate equations, nuclear processes that lead to the formation of the noble gases He, Ne, Ar, Kr, Xe, and Rn. (*Hint:* Helium is formed from radioactive decay, neon is formed from the positron emission of  $^{22}\text{Na}$ , the formation of Ar, Xe, and Rn are discussed in the chapter, and Kr is produced from the fission of  $^{235}\text{U}$ .)

- 21.88** Write an essay on the pros and cons of nuclear power (based on nuclear fission), paying particular attention to its effect on global warming, nuclear reactor safety and weapon risks, and nuclear waste disposal.

- 21.89** The half-life of  $^{27}\text{Mg}$  is 9.50 min. (a) Initially there were  $4.20 \times 10^{12}$   $^{27}\text{Mg}$  nuclei present. How many  $^{27}\text{Mg}$  nuclei are left 30.0 min later? (b) Calculate the  $^{27}\text{Mg}$  activities (in Ci) at  $t = 0$  and  $t = 30.0$  min. (c) What is the probability that any one  $^{27}\text{Mg}$  nucleus decays during a 1-s interval? What assumption is made in this calculation?

- 21.90** The radioactive isotope  $^{238}\text{Pu}$ , used in pacemakers, decays by emitting an alpha particle with a half-life of 86 yr. (a) Write an equation for the decay process. (b) The energy of the emitted alpha particle is  $9.0 \times 10^{-13}$  J, which is the energy per decay. Assume that all the alpha particle energy is used to run the pacemaker, calculate the power output at  $t = 0$  and

$t = 10$  yr. Initially 1.0 mg of  $^{238}\text{Pu}$  was present in the pacemaker. (*Hint:* After 10 yr, the activity of the isotope decreases by 8.0 percent. Power is measured in watts or J/s.).

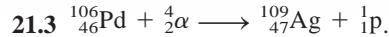
- 21.91** (a) Assume nuclei are spherical in shape, show that its radius ( $r$ ) is proportional to the cube root of mass number ( $A$ ). (b) In general, the radius of a nucleus is given by  $r = r_0 A^{\frac{1}{3}}$ , where  $r_0$ , the proportionality constant, is given by  $1.2 \times 10^{-15}$  m. Calculate the volume of the  $^{238}\text{U}$  nucleus.

- 21.92** The quantity of a radioactive material is often measured by its activity (measured in curies or millicuries) rather than by its mass. In a brain scan procedure, a 70-kg patient is injected with 20.0 mCi of  $^{99m}\text{Tc}$ , which decays by emitting  $\gamma$ -ray photons with a half-life of 6.0 h. Given that the RBE of these photons is 0.98 and only two-thirds of the photons are absorbed by the body, calculate the rem dose received by the patient. Assume all of the  $^{99m}\text{Tc}$  nuclei decay while in the body. The energy of a gamma photon is  $2.29 \times 10^{-14}$  J.

- 21.93** Modern designs of atomic bombs contain, in addition to uranium or plutonium, small amounts of tritium and deuterium to boost the power of explosion. What is the role of tritium and deuterium in these bombs?

## ANSWERS TO PRACTICE EXERCISES

**21.1**  $^{78}_{34}\text{Se}$ .    **21.2**  $2.63 \times 10^{-10}$  J;  $1.26 \times 10^{-12}$  J/nucleon.



The strength of one kind of polymer called Lexan is so great that it is used to make bullet-proof windows.

CHAPTER

# 22



## Organic Polymers—Synthetic and Natural

### CHAPTER OUTLINE

- 22.1** Properties of Polymers 740
- 22.2** Synthetic Organic Polymers 740
  - Addition Reactions • Condensation Reactions
- 22.3** Proteins 744
  - Amino Acids • Protein Structure
- 22.4** Nucleic Acids 752

### ESSENTIAL CONCEPTS

**Synthetic Organic Polymers** Many organic polymers have been synthesized by various chemical processes. They mimic and sometimes surpass the properties of those that occur naturally. Nylon is the best known of all synthetic organic polymers.

**Proteins** Proteins are natural polymers made of amino acids. They perform a host of functions ranging from catalysis, transport and storage of vital substances, coordinated motion, and protection against diseases. The complex structures of proteins have been analyzed in terms of their primary, secondary, tertiary, and quaternary structures. The three-dimensional integrity of protein molecules is maintained by various intermolecular forces and hydrogen bonding.

**Nucleic Acids** Deoxyribonucleic acid (DNA) carries all the genetic information, and ribonucleic acid (RNA) controls the synthesis of proteins. The elucidation of the double helical structure of DNA is one of the major accomplishments in science in the twentieth century.



### Activity Summary

1. Interactivity: Synthetic Organic Polymers (22.2)
2. Interactivity: The World of Polymers (22.2)

## 22.1 Properties of Polymers

A **polymer** is a molecular compound distinguished by a high molar mass, ranging into thousands and millions of grams, and made up of many repeating units. The physical properties of these so-called macromolecules differ greatly from those of small, ordinary molecules, and special techniques are required to study them.

Naturally occurring polymers include proteins, nucleic acids, cellulose (polysaccharides), and rubber (polyisoprene). Most synthetic polymers are organic compounds. Familiar examples are nylon, poly(hexamethylene adipamide); Dacron, poly(ethylene terephthalate); and Lucite or Plexiglas, poly(methyl methacrylate).

The development of polymer chemistry began in the 1920s with the investigation into a puzzling behavior of certain materials, including wood, gelatin, cotton, and rubber. For example, when rubber, with the known empirical formula of  $C_5H_8$ , was dissolved in an organic solvent, the solution displayed several unusual properties—high viscosity, low osmotic pressure, and negligible freezing-point depression. These observations strongly suggested the presence of solutes of very high molar mass, but chemists were not ready at that time to accept the idea that such giant molecules could exist. Instead, they postulated that materials such as rubber consist of aggregates of small molecular units, like  $C_5H_8$  or  $C_{10}H_{16}$ , held together by intermolecular forces. This misconception persisted for a number of years, until the German chemist Hermann Staudinger clearly showed that these so-called aggregates are, in fact, enormously large molecules, each of which contains many thousands of atoms held together by covalent bonds.

Once the structures of these macromolecules were understood, the way was open for manufacturing polymers, which now pervade almost every aspect of our daily lives. About 90 percent of today's chemists, including biochemists, work with polymers.



**Interactivity:**  
Synthetic Organic Polymers  
ARIS, Interactives

**Interactivity:**  
The World of Polymers  
ARIS, Interactives

## 22.2 Synthetic Organic Polymers

Because of their size, we might expect molecules containing thousands of carbon and hydrogen atoms to form an enormous number of structural and geometric isomers (if  $C=C$  bonds are present). However, these molecules are made up of **monomers**, *simple repeating units*, and this type of composition severely restricts the number of possible isomers. Synthetic polymers are created by joining monomers together, one at a time, by means of addition reactions and condensation reactions.

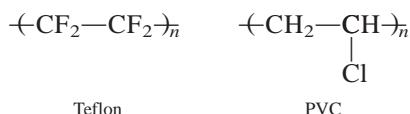
### Addition Reactions

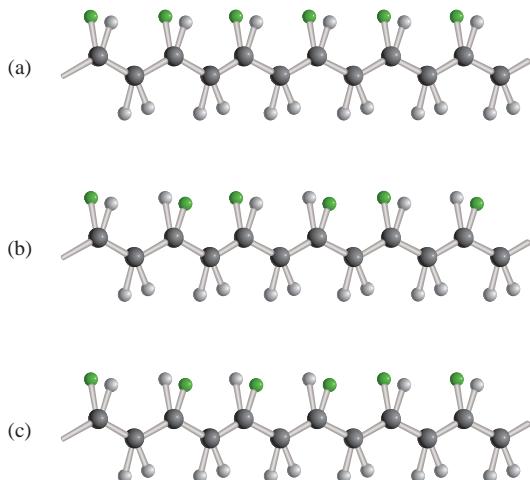
Addition reactions were described on p. 367.

Addition reactions involve unsaturated compounds containing double or triple bonds, particularly  $C=C$  and  $C\equiv C$ . Hydrogenation and reactions of hydrogen halides and halogens with alkenes and alkynes are examples of addition reactions.

In Chapter 11 we saw that polyethylene is formed by addition reaction. Polyethylene is an example of a **homopolymer**, which is a polymer made up of only one type of monomer. Other homopolymers that are synthesized by the radical mechanism are Teflon, polytetrafluoroethylene and poly(vinyl chloride) (PVC):

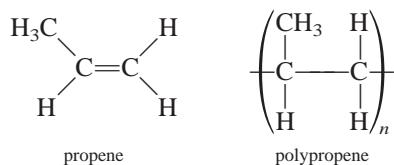
*n* is in the hundreds or thousands.





**Figure 22.1**  
Stereoisomers of polymers.  
When the R group (green sphere) is  $\text{CH}_3$ , the polymer is polypropene. (a) When the R groups are all on one side of the chain, the polymer is said to be isotactic. (b) When the R groups alternate from side to side, the polymer is said to be syndiotactic. (c) When the R groups are disposed at random, the polymer is atactic.

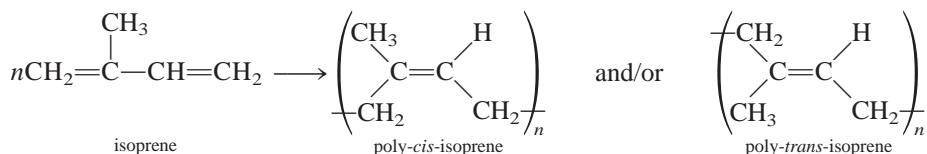
The chemistry of polymers is more complex if the starting units are asymmetric:



Several different structures can result from an addition reaction of propenes (Figure 22.1). If the additions occur randomly, we obtain *atactic* polypropenes, which do not pack together well. These polymers are rubbery, amorphous, and relatively weak. Two other possibilities are an *isotactic* structure, in which the R groups are all on the same side of the asymmetric carbon atoms, and a *syndiotactic* form, in which the R groups alternate on the left and right of the asymmetric carbons. Of these, the isotactic isomer has the highest melting point and greatest crystallinity and is endowed with superior mechanical properties.

Rubber is probably the best known organic polymer and the only true hydrocarbon polymer found in nature. It is formed by the radical addition of the monomer isoprene. Actually, polymerization can result in either poly-*cis*-isoprene or poly-*trans*-isoprene—or a mixture of both, depending on reaction conditions:

**Stereoisomerism was discussed in Section 20.4.**

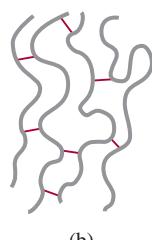


Note that in the *cis* isomer the two CH<sub>2</sub> groups are on the same side of the C=C bond, whereas the same groups are across from each other in the *trans* isomer. Natural rubber is poly-*cis*-isoprene, which is extracted from the tree *Hevea brasiliensis* (Figure 22.2).

An unusual and very useful property of rubber is its elasticity. Rubber will stretch up to 10 times its length and, if released, will return to its original size. In contrast, a piece of copper wire can be stretched only a small percentage of its length and still return to its original size. Unstretched rubber is amorphous. Stretched rubber, however, possesses a fair amount of crystallinity and order.

**Figure 22.2**

*Latex (aqueous suspension of rubber particles) being collected from a rubber tree.*

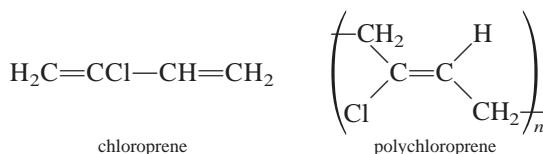
**Figure 22.3**

*Rubber molecules ordinarily are bent and convoluted. Parts (a) and (b) represent the long chains before and after vulcanization, respectively; (c) shows the alignment of molecules when stretched. Without vulcanization these molecules would slip past one another, and rubber's elastic properties would be gone.*



The elastic property of rubber is due to the flexibility of the long-chain molecules. In the bulk state, however, rubber is a tangle of polymeric chains, and if the external force is strong enough, individual chains slip past one another, thereby causing the rubber to lose most of its elasticity. In 1839, the American chemist Charles Goodyear discovered that natural rubber could be cross-linked with sulfur (using zinc oxide as the catalyst) to prevent chain slippage (Figure 22.3). His process, known as *vulcanization*, paved the way for many practical and commercial uses of rubber, such as in automobile tires and dentures.

During World War II a shortage of natural rubber in the United States prompted an intensive program to produce synthetic rubber. Most synthetic rubbers (called *elastomers*) are made from petroleum products such as ethylene, propene, and butadiene. For example, chloroprene molecules polymerize readily to form polychloroprene, commonly known as *neoprene*, which has properties that are comparable or even superior to those of natural rubber:



Another important synthetic rubber is formed by the addition of butadiene to styrene in a 3:1 ratio to give styrene-butadiene rubber (SBR). Because styrene and butadiene are different monomers, SBR is called a *copolymer*, which is a polymer containing two or more different monomers. Table 22.1 shows a number of common and familiar homopolymers and one copolymer produced by addition reactions.

## Condensation Reactions

One of the best-known polymer condensation processes is the reaction between hexamethylenediamine and adipic acid, shown in Figure 22.4. The final product, called nylon 66 (because there are six carbon atoms each in hexamethylenediamine and adipic acid), was first made by the American chemist Wallace Carothers at DuPont in

Condensation reaction was defined on p. 376.

**TABLE 22.1** Some Monomers and Their Common Synthetic Polymers

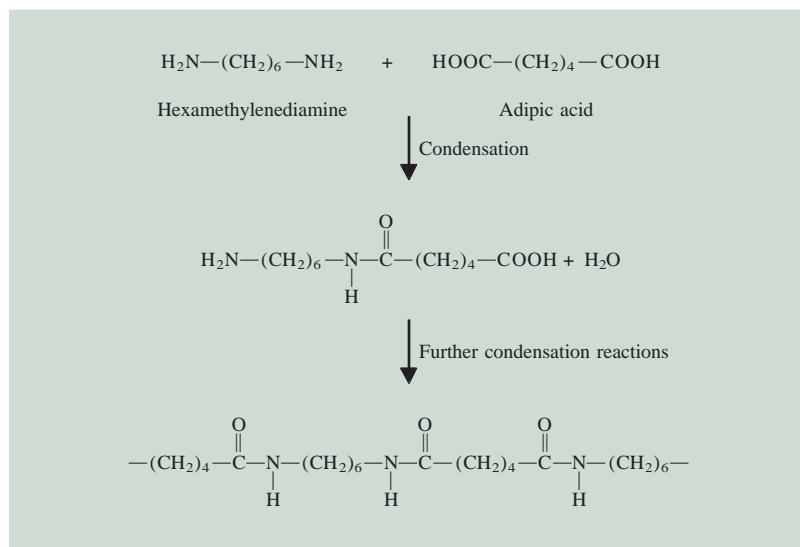
| Monomer  |                          | Polymer  |   |
|--|--------------------------|--|---|
| Formula  | Name                     | Name and Formula   | Uses  |
| $\text{H}_2\text{C}=\text{CH}_2$   | Ethylene                 | Polyethylene<br>$-(\text{CH}_2-\text{CH}_2)_n$   | Plastic piping,<br>bottles,<br>electrical<br>insulation, toys                       |
| $\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C} \\   \\ \text{CH}_3 \end{array}$                                  | Propene                  | Polypropene<br>$\left(\begin{array}{c} \text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2 \\   \qquad   \\ \text{CH}_3 \qquad \text{CH}_3 \end{array}\right)_n$ | Packaging film,<br>carpets, crates<br>for soft-drink<br>bottles, lab<br>wares, toys |
| $\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C} \\   \\ \text{Cl} \\   \\ \text{H} \\   \\ \text{CN} \end{array}$ | Vinyl chloride           | Poly(vinyl chloride) (PVC)<br>$-(\text{CH}_2-\text{CH})_n$   | Piping, siding,<br>gutters, floor<br>tile, clothing,<br>toys                        |
| $\begin{array}{c} \text{H}_2\text{C}=\text{C} \\   \\ \text{CN} \end{array}$   | Acrylonitrile            | Polyacrylonitrile (PAN)<br>$\left(\begin{array}{c} \text{CH}_2-\text{CH} \\   \\ \text{CN} \end{array}\right)_n$   | Carpets, knitwear   |
| $\text{F}_2\text{C}=\text{CF}_2$   | Tetrafluoro-<br>ethylene | Polytetrafluoroethylene<br>(Teflon)<br>$-(\text{CF}_2-\text{CF}_2)_n$  | Coating on<br>cooking<br>utensils,<br>electrical<br>insulation,<br>bearings         |
| $\begin{array}{c} \text{COOCH}_3 \\   \\ \text{H}_2\text{C}=\text{C} \\   \\ \text{CH}_3 \end{array}$                            | Methyl<br>methacrylate   | Poly(methyl methacrylate)<br>(Plexiglas)<br>$-(\text{CH}_2-\text{C})_n$  | Optical<br>equipment,<br>home<br>furnishing   |
| $\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C} \\   \\ \text{C}_6\text{H}_5 \end{array}$                         | Styrene                  | Polystyrene<br>$-(\text{CH}_2-\text{CH})_n$  | Containers,<br>thermal<br>insulation (ice<br>buckets, water<br>coolers), toys       |
| $\begin{array}{c} \text{H} \qquad \text{H} \\   \qquad   \\ \text{H}_2\text{C}=\text{C}-\text{C}=\text{CH}_2 \end{array}$        | Butadiene                | Polybutadiene<br>$-(\text{CH}_2\text{CH}=\text{CHCH}_2)_n$   | Tire tread, coating<br>resin  |
| See above<br>structures  | Butadiene and<br>styrene | Styrene-butadiene rubber<br>(SBR)<br>$-(\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_n$  | Synthetic rubber  |



Bubble gums contain synthetic styrene-butadiene rubber.

**Figure 22.5**

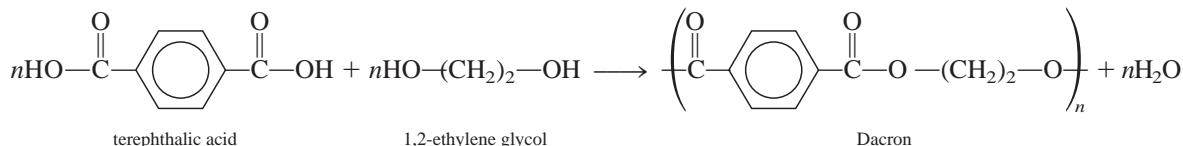
The nylon rope trick. Adding a solution of adipoyl chloride (an adipic acid derivative in which the OH groups have been replaced by Cl groups) in cyclohexane to an aqueous solution of hexamethylenediamine causes nylon to form at the interface of the two solutions, which do not mix. It can then be drawn off.

**Figure 22.4**

The formation of nylon by the condensation reaction between hexamethylenediamine and adipic acid.

1931. The versatility of nylons is so great that the annual production of nylons and related substances now amounts to several billion pounds. Figure 22.5 shows how nylon 66 is prepared in the laboratory.

Condensation reactions are also used in the manufacture of Dacron (polyester)



Polyesters are used in fibers, films, and plastic bottles.

## 22.3 Proteins

| 1A | 2A | 3A | 4A | 5A | 6A | 7A | 8A |
|----|----|----|----|----|----|----|----|
| H  |    | C  | N  | O  |    | S  |    |
|    |    |    |    |    |    |    |    |
|    |    |    |    |    |    |    |    |
|    |    |    |    |    |    |    |    |

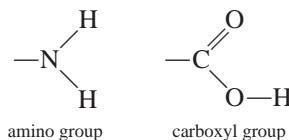
Elements in proteins.

**Proteins** are polymers of amino acids; they play a key role in nearly all biological processes. Enzymes, the catalysts of biochemical reactions, are mostly proteins. Proteins also facilitate a wide range of other functions, such as transport and storage of vital substances, coordinated motion, mechanical support, and protection against diseases. The human body contains an estimated 100,000 different kinds of proteins, each of which has a specific physiological function. As we will see in this section, the chemical composition and structure of these complex natural polymers are the basis of their specificity.

### Amino Acids

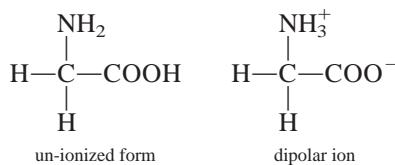
Proteins have high molar masses, ranging from about 5000 g to  $1 \times 10^7$  g, and yet the percent composition by mass of the elements in proteins is remarkably constant: carbon, 50 to 55 percent; hydrogen, 7 percent; oxygen, 23 percent; nitrogen, 16 percent; and sulfur, 1 percent.

The basic structural units of proteins are *amino acids*. An ***amino acid*** is a compound that contains at least one amino group ( $-NH_2$ ) and at least one carboxyl group ( $-COOH$ ):

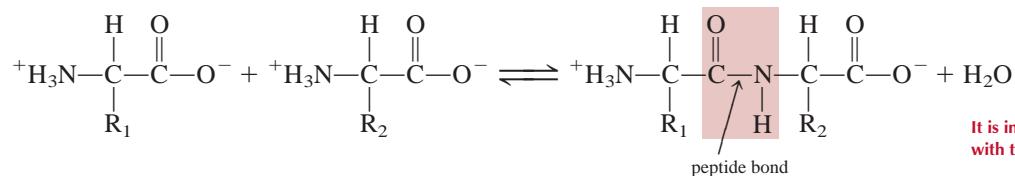


Twenty different amino acids are the building blocks of all the proteins in the human body. Table 22.2 shows the structures of these vital compounds, along with their three-letter abbreviations.

Amino acids in solution at neutral pH exist as *dipolar ions*, meaning that the proton on the carboxyl group has migrated to the amino group. Consider glycine, the simplest amino acid. The un-ionized form and the dipolar ion of glycine are shown here:



The first step in the synthesis of a protein molecule is a condensation reaction between an amino group on one amino acid and a carboxyl group on another amino acid. The molecule formed from the two amino acids is called a *dipeptide*, and the bond joining them together is a *peptide bond*:



where  $R_1$  and  $R_2$  represent a H atom or some other group;  $-CO-NH-$  is called the *amide group*. Because the equilibrium of the reaction joining two amino acids lies to the left, the process is coupled to the hydrolysis of ATP (see p. 633).

Either end of a dipeptide can engage in a condensation reaction with another amino acid to form a *tripeptide*, a *tetrapeptide*, and so on. The final product, the protein molecule, is a *polypeptide*; it can also be thought of as a polymer of amino acids.

An amino acid unit in a polypeptide chain is called a *residue*. Typically, a polypeptide chain contains 100 or more amino acid residues. The sequence of amino acids in a polypeptide chain is written conventionally from left to right, starting with the amino-terminal residue and ending with the carboxyl-terminal residue. Let us consider a dipeptide formed from glycine and alanine. Figure 22.6 shows that alanyl-glycine and glycylalanine are different molecules. With 20 different amino acids to choose from,  $20^2$ , or 400, different dipeptides can be generated. Even for a very small protein such as insulin, which contains only 50 amino acid residues, the number of chemically different structures that is possible is of the order of  $20^{50}$  or  $10^{65}$ ! This is an incredibly large number when you consider that the total number of atoms in our galaxy is about  $10^{68}$ . With so many possibilities for protein synthesis, it is remarkable that generation after generation of cells can produce identical proteins for specific physiological functions.

**TABLE 22.2** The 20 Amino Acids Essential to Living Organisms\*

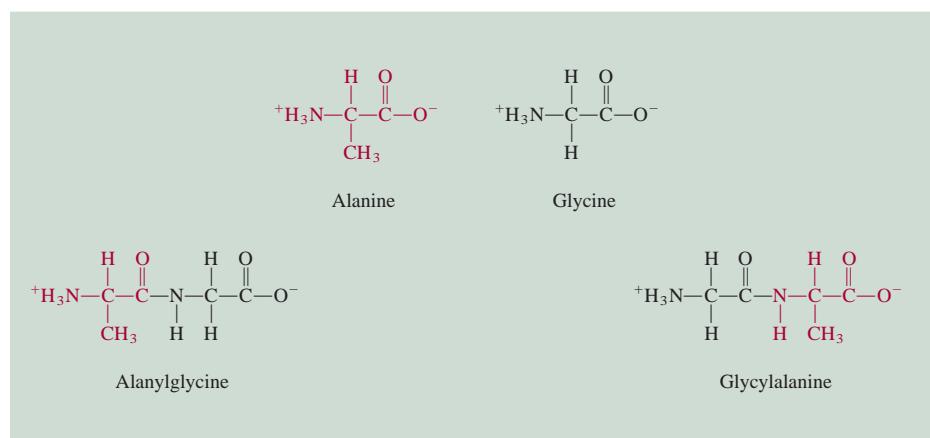
| Name          | Abbreviation | Structure  |
|---------------|--------------|--|
| Alanine       | Ala          | <p>The structure shows a central carbon atom bonded to four groups: a methyl group (<math>\text{H}_3\text{C}</math>) on top, a hydrogen atom (<math>\text{H}</math>) on the right, an amino group (<math>\text{NH}_3^+</math>) on the bottom, and a carboxylate group (<math>\text{COO}^-</math>) on the left.</p> |
| Arginine      | Arg          | <p>The structure shows a guanidino group (<math>\text{H}_2\text{N}-\text{C}(=\text{NH})-\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}(=\text{NH})-\text{NH}_3^+</math>) attached to a carboxylate group (<math>\text{COO}^-</math>).</p>   |
| Asparagine    | Asn          | <p>The structure shows an amide group (<math>\text{H}_2\text{N}-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{NH})-\text{NH}_3^+</math>) attached to a carboxylate group (<math>\text{COO}^-</math>).</p>  |
| Aspartic acid | Asp          | <p>The structure shows a di-carboxylic acid group (<math>\text{HOOC}-\text{CH}_2-\text{C}(=\text{NH})-\text{NH}_3^+</math>) attached to a carboxylate group (<math>\text{COO}^-</math>).</p>   |
| Cysteine      | Cys          | <p>The structure shows a thiomethyl group (<math>\text{HS}-\text{CH}_2-\text{C}(=\text{NH})-\text{NH}_3^+</math>) attached to a carboxylate group (<math>\text{COO}^-</math>).</p>   |
| Glutamic acid | Glu          | <p>The structure shows a di-carboxylic acid group (<math>\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{C}(=\text{NH})-\text{NH}_3^+</math>) attached to a carboxylate group (<math>\text{COO}^-</math>).</p>   |
| Glutamine     | Gln          | <p>The structure shows an amide group (<math>\text{H}_2\text{N}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2-\text{C}(=\text{NH})-\text{NH}_3^+</math>) attached to a carboxylate group (<math>\text{COO}^-</math>).</p>  |
| Glycine       | Gly          | <p>The structure shows a methyl group (<math>\text{H}-\text{CH}_2-</math>) attached to a carboxylate group (<math>\text{COO}^-</math>).</p>  |
| Histidine     | His          | <p>The structure shows an imidazole ring system (<math>\text{HC}=\text{C}-\text{CH}_2-\text{C}(=\text{NH})-\text{NH}_3^+</math>) attached to a carboxylate group (<math>\text{COO}^-</math>).</p>  |
| Isoleucine    | Ile          | <p>The structure shows a branched chain (<math>\text{H}_3\text{C}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{C}(=\text{NH})-\text{NH}_3^+</math>) attached to a carboxylate group (<math>\text{COO}^-</math>).</p>   |

(Continued)

\*The shaded portion is the R group of the amino acid. The amino acids are shown as dipolar ions.

**TABLE 22.2** The 20 Amino Acids Essential to Living Organisms—Cont.

| Name          | Abbreviation | Structure   |
|---------------|--------------|---|
| Leucine       | Leu          | The structure shows a central alpha-carbon bonded to a hydrogen atom, an amino group (NH3+), a carboxylate group (COO-), and a beta-carbon. The beta-carbon is bonded to two methyl groups (H3C).   |
| Lysine        | Lys          | The structure shows a central alpha-carbon bonded to a hydrogen atom, an amino group (NH3+), a carboxylate group (COO-), and a beta-carbon. The beta-carbon is bonded to three methylene groups (CH2).  |
| Methionine    | Met          | The structure shows a central alpha-carbon bonded to a hydrogen atom, an amino group (NH3+), a carboxylate group (COO-), and a beta-carbon. The beta-carbon is bonded to a methyl group (H3C) and a sulfur atom, which is further bonded to a methylene group (CH2).                                |
| Phenylalanine | Phe          | The structure shows a central alpha-carbon bonded to a hydrogen atom, an amino group (NH3+), a carboxylate group (COO-), and a beta-carbon. The beta-carbon is bonded to a phenyl ring (C6H5) and a methylene group (CH2).  |
| Proline       | Pro          | The structure shows a central alpha-carbon bonded to a hydrogen atom, an amino group (NH3+), a carboxylate group (COO-), and a beta-carbon. The beta-carbon is bonded to a methylene group (CH2) and a nitrogen atom, which is part of a five-membered imidazole ring.                              |
| Serine        | Ser          | The structure shows a central alpha-carbon bonded to a hydrogen atom, an amino group (NH3+), a carboxylate group (COO-), and a beta-carbon. The beta-carbon is bonded to a hydroxyl group (OH).   |
| Threonine     | Thr          | The structure shows a central alpha-carbon bonded to a hydrogen atom, an amino group (NH3+), a carboxylate group (COO-), and a beta-carbon. The beta-carbon is bonded to a methyl group (H3C) and a hydroxyl group (OH).  |
| Tryptophan    | Trp          | The structure shows a central alpha-carbon bonded to a hydrogen atom, an amino group (NH3+), a carboxylate group (COO-), and a beta-carbon. The beta-carbon is bonded to a methyl group (H3C) and a double-bonded carbon atom, which is further bonded to a phenyl ring (C6H5) and a hydrogen atom. |
| Tyrosine      | Tyr          | The structure shows a central alpha-carbon bonded to a hydrogen atom, an amino group (NH3+), a carboxylate group (COO-), and a beta-carbon. The beta-carbon is bonded to a hydroxyl group (OH) and a phenyl ring (C6H4).  |
| Valine        | Val          | The structure shows a central alpha-carbon bonded to a hydrogen atom, an amino group (NH3+), a carboxylate group (COO-), and a beta-carbon. The beta-carbon is bonded to two methyl groups (H3C).   |

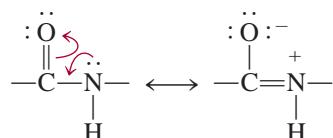


**Figure 22.6**

The formation of two dipeptides from two different amino acids. Alanyl glycine is different from glycylalanine in that in alanyl glycine the amino and methyl groups are bonded to the same carbon atom.

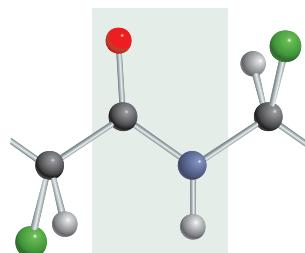
## Protein Structure

The type and number of amino acids in a given protein along with the sequence or order in which these amino acids are joined together determine the protein's structure. In the 1930s Linus Pauling and his coworkers conducted a systematic investigation of protein structure. First they studied the geometry of the basic repeating group, that is, the amide group, which is represented by the following resonance structures:



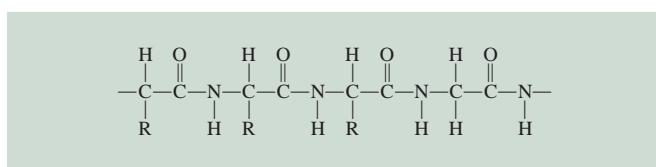
Because it is more difficult (that is, it would take more energy) to twist a double bond than a single bond, the four atoms in the amide group become locked in the same plane (Figure 22.7). Figure 22.8 depicts the repeating amide group in a polypeptide chain.

On the basis of models and X-ray diffraction data, Pauling deduced that there are two common structures for protein molecules, called the  $\alpha$  helix and the  $\beta$ -pleated sheet. The  $\alpha$ -helical structure of a polypeptide chain is shown in Figure 22.9. The



**Figure 22.7**

The planar amide group in protein. Rotation about the peptide bond in the amide group is hindered by its double-bond character. The black atoms represent carbon; blue, nitrogen; red, oxygen; green, R group; and gray, hydrogen.



**Figure 22.8**

A polypeptide chain. Note the repeating units of the amide group. The symbol R represents part of the structure characteristic of the individual amino acids. For glycine, R is simply a H atom.

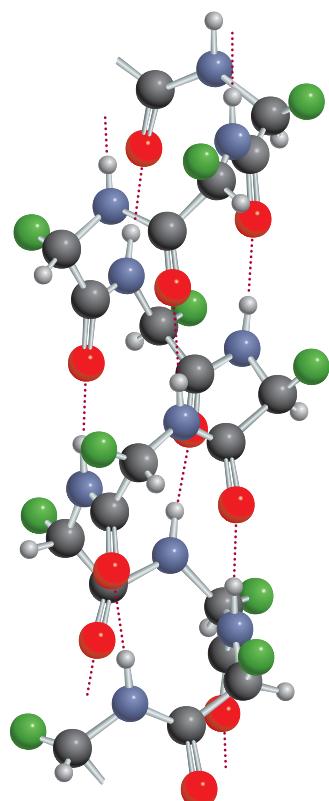
helix is stabilized by *intramolecular* hydrogen bonds between the NH and CO groups of the main chain, giving rise to an overall rodlike shape. The CO group of each amino acid is hydrogen-bonded to the NH group of the amino acid that is four residues away in the sequence. In this manner all the main-chain CO and NH groups take part in hydrogen bonding. X-ray studies have shown that the structure of a number of proteins, including myoglobin and hemoglobin, is to a great extent  $\alpha$ -helical in nature.

The  $\beta$ -pleated structure is markedly different from the  $\alpha$  helix in that it is like a sheet rather than a rod. The polypeptide chain is almost fully extended, and each chain forms many *intermolecular* hydrogen bonds with adjacent chains. Figure 22.10 shows the two different types of  $\beta$ -pleated structures, called *parallel* and *antiparallel*. Silk molecules possess the  $\beta$  structure. Because its polypeptide chains are already in extended form, silk lacks elasticity and extensibility, but it is quite strong due to the many intermolecular hydrogen bonds.

It is customary to divide protein structure into four levels of organization. The *primary structure* refers to the unique amino acid sequence of the polypeptide chain. The *secondary structure* includes those parts of the polypeptide chain that are stabilized by a regular pattern of hydrogen bonds between the CO and NH groups of the backbone, for example, the  $\alpha$  helix. The term *tertiary structure* applies to the three-dimensional structure stabilized by dispersion forces, hydrogen bonding, and other intermolecular forces. It differs from secondary structure in that the amino acids taking part in these interactions may be far apart in the polypeptide chain. A protein molecule may be made up of more than one polypeptide chain. Thus, in addition to the various interactions *within* a chain that give rise to the secondary and tertiary structures, we must also consider the interaction *between* chains. The overall arrangement of the polypeptide chains is called the *quaternary structure*. For example, the hemoglobin molecule consists of four separate polypeptide chains, or *subunits*. These subunits are held together by van der Waals forces and ionic forces (Figure 22.11).

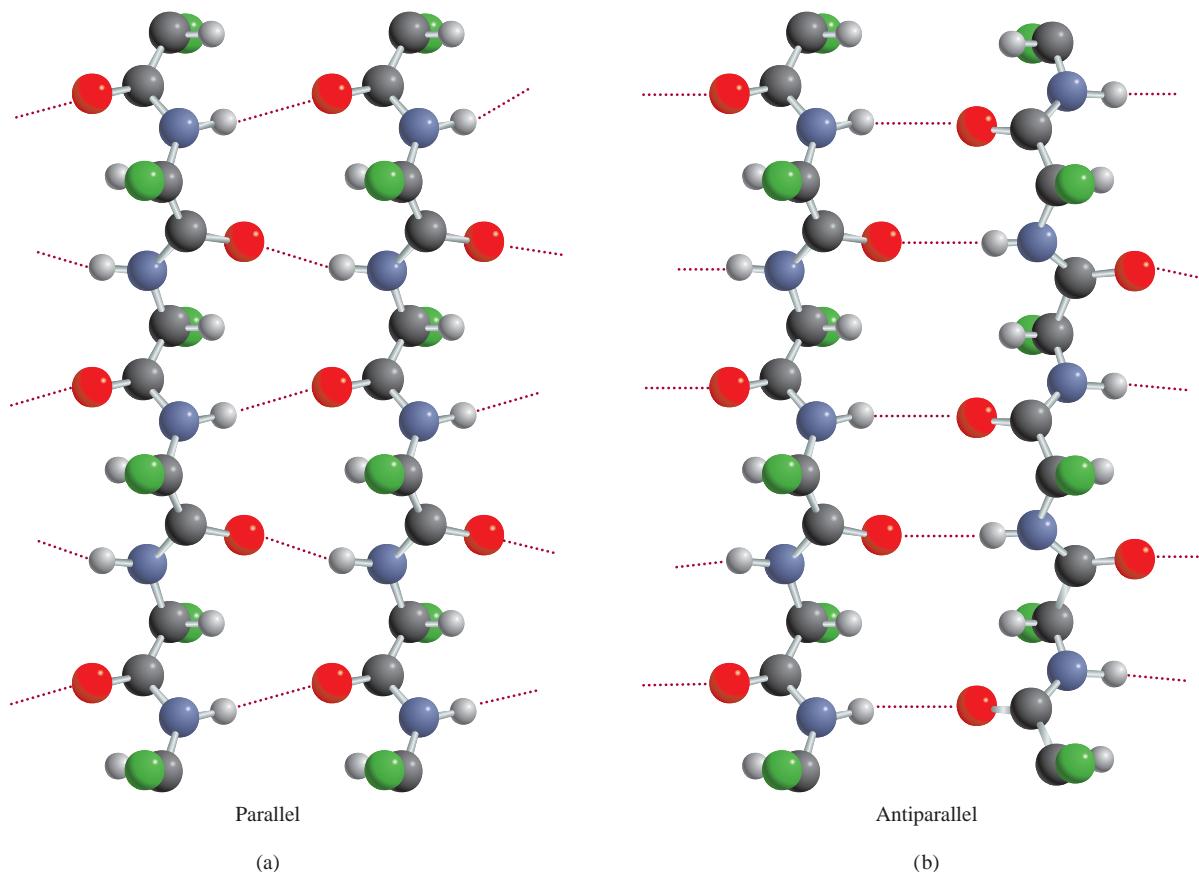
Pauling's work was a great triumph in protein chemistry. It showed for the first time how to predict a protein structure purely from a knowledge of the geometry of its fundamental building blocks—amino acids. However, there are many proteins whose structures do not correspond to the  $\alpha$ -helical or  $\beta$  structure. Chemists now know that the three-dimensional structures of these biopolymers are maintained by several types of intermolecular forces in addition to hydrogen bonding (Figure 22.12). The delicate balance of the various interactions can be appreciated by considering an example: When glutamic acid, one of the amino acid residues in two of the four polypeptide chains in hemoglobin, is replaced by valine, another amino acid, the protein molecules aggregate to form insoluble polymers, causing the disease known as sickle cell anemia.

In spite of all the forces that give proteins their structural stability, most proteins have a certain amount of flexibility. Enzymes, for example, are flexible enough to change their geometry to fit substrates of various sizes and shapes. Another interesting example of protein flexibility is found in the binding of hemoglobin to oxygen. Each of the four polypeptide chains in hemoglobin contains a heme group that can bind to an oxygen molecule (see Section 20.6). In deoxyhemoglobin, the affinity of each of the heme groups for oxygen is about the same. However, as soon as one of the heme groups becomes oxygenated, the affinity of the other three hemes for oxygen is greatly enhanced. This phenomenon, called *cooperativity*, makes hemoglobin a particularly suitable substance for the uptake of oxygen in the lungs. By the same token, once a fully oxygenated hemoglobin molecule releases an oxygen molecule (to myoglobin in the tissues), the other three oxygen molecules will depart with



**Figure 22.9**

The  $\alpha$ -helical structure of a polypeptide chain. The structure is held in position by intramolecular hydrogen bonds, shown as dotted lines. For color key, see Fig. 22.7.



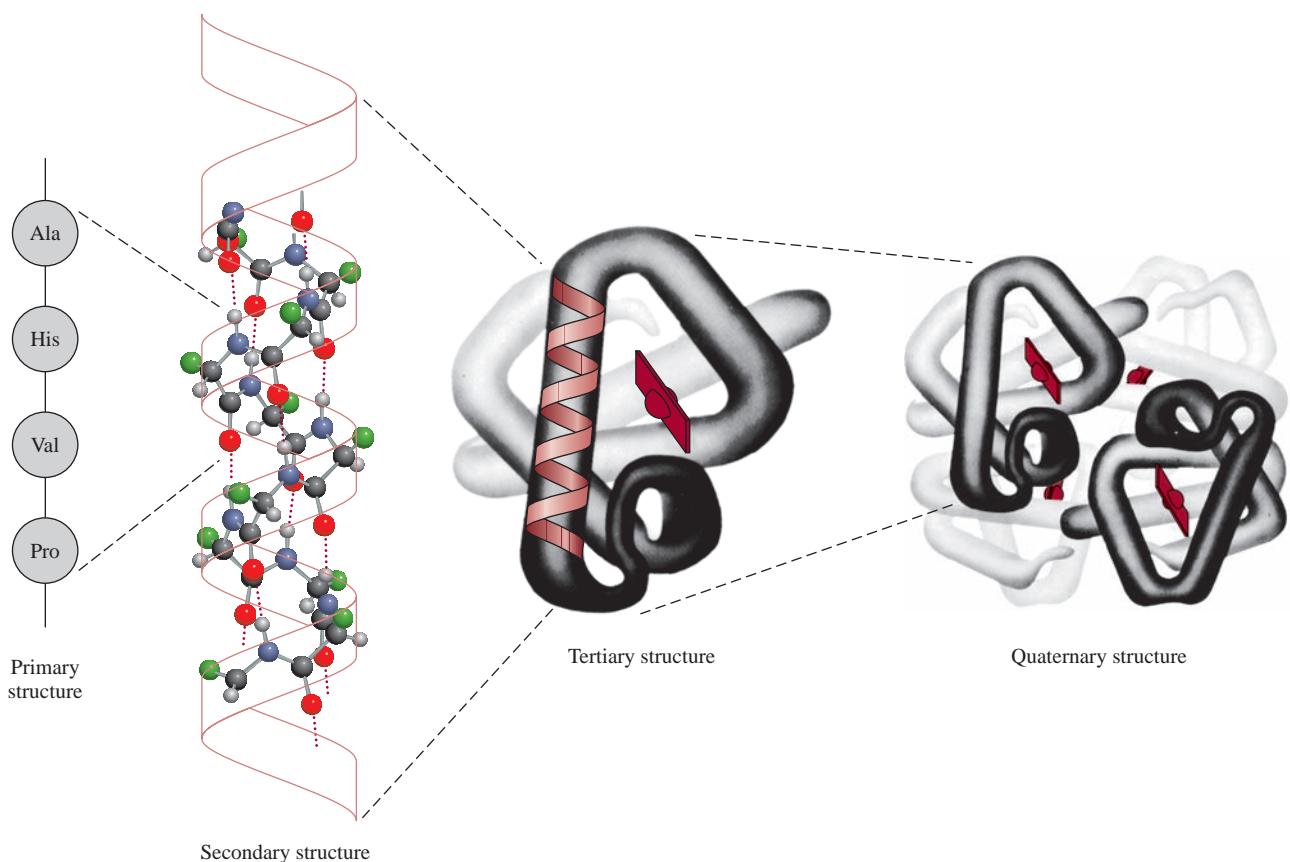
**Figure 22.10**

**Figure 22.16** Hydrogen bonds (*a*) in a parallel  $\beta$ -pleated sheet structure, in which all the polypeptide chains are oriented in the same direction, and (*b*) in an antiparallel  $\beta$ -pleated sheet, in which adjacent polypeptide chains run in opposite directions. For color key, see Fig. 22.7.

increasing ease. The cooperative nature of the binding is such that information about the presence (or absence) of oxygen molecules is transmitted from one subunit to another along the polypeptide chains, a process made possible by the flexibility of the three-dimensional structure (Figure 22.13). It is believed that the  $\text{Fe}^{2+}$  ion has too large a radius to fit into the porphyrin ring of deoxyhemoglobin. When  $\text{O}_2$  binds to  $\text{Fe}^{2+}$ , however, the ion shrinks somewhat so that it can fit into the plane of the ring. As the ion slips into the ring, it pulls the histidine residue toward the ring and thereby sets off a sequence of structural changes from one subunit to another. Although the details of the changes are not clear, biochemists believe that this is how the binding of an oxygen molecule to one heme group affects another heme group. The structural changes drastically affect the affinity of the remaining heme groups for oxygen molecules.

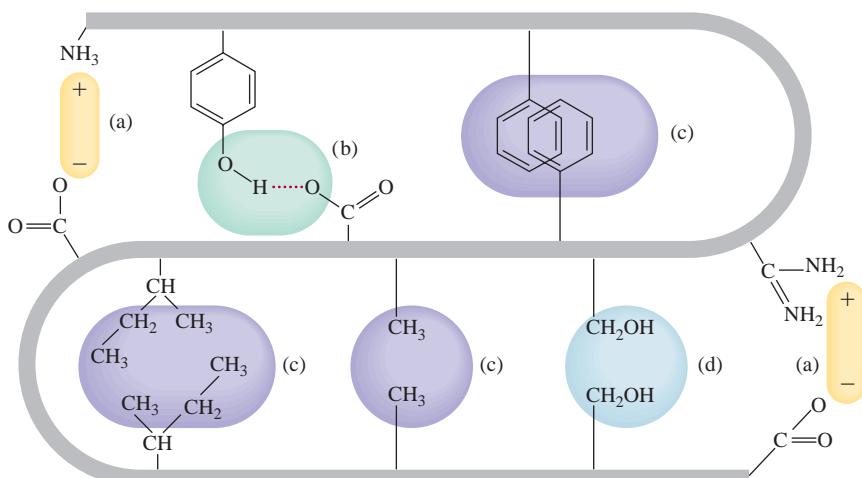
When proteins are heated above body temperature or when they are subjected to unusual acid or base conditions or treated with special reagents called *denaturants*, they lose some or all of their tertiary and secondary structure. Called ***denatured proteins***, proteins in this state *no longer exhibit normal biological activities*. Figure 22.14 shows the variation of rate with temperature for a typical enzyme-catalyzed reaction.

**Hard-boiling an egg denatures the proteins in the egg white.**

**Figure 22.11**

The primary, secondary, tertiary, and quaternary structure of the hemoglobin molecule.

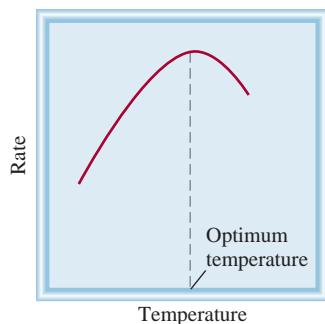
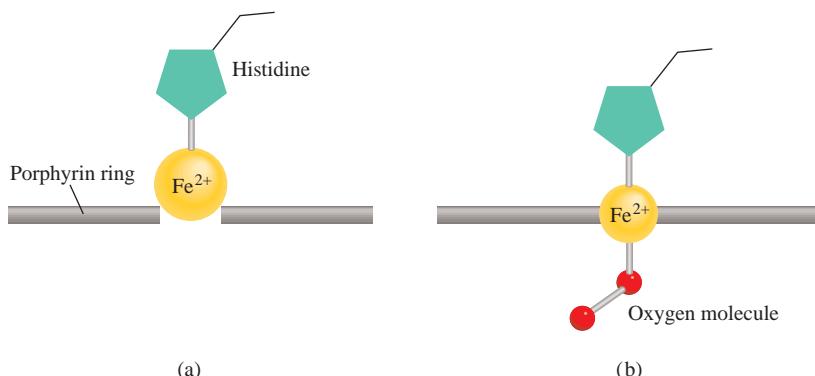
Initially, the rate increases with increasing temperature, as we would expect. Beyond the optimum temperature, however, the enzyme begins to denature and the rate falls rapidly. If a protein is denatured under mild conditions, its original structure can often be regenerated by removing the denaturant or by restoring the temperature to normal conditions. This process is called *reversible denaturation*.

**Figure 22.12**

Intermolecular forces in a protein molecule: (a) ionic forces, (b) hydrogen bonding, (c) dispersion forces, and (d) dipole-dipole forces.

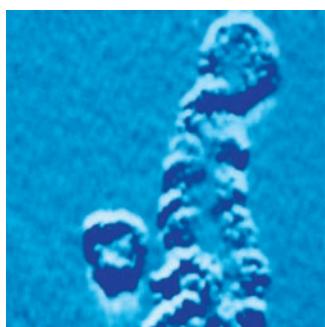
**Figure 22.13**

The structural changes that occur when the heme group in hemoglobin binds to an oxygen molecule. (a) The heme group in deoxyhemoglobin. (b) Oxyhemoglobin.

**Figure 22.14**

Dependence of the rate of an enzyme-catalyzed reaction on temperature. Above the optimum temperature at which an enzyme is most effective, its activity drops off as a consequence of denaturation.

If the DNA molecules from all the cells in a human were stretched and joined end to end, the length would be about 100 times the distance to the sun!



An electron micrograph of a DNA molecule. The double-helical structure is evident.

## 22.4 Nucleic Acids

**Nucleic acids** are high-molar-mass polymers that play an essential role in protein synthesis. **Deoxyribonucleic acid (DNA)** and **ribonucleic acid (RNA)** are the two types of nucleic acid. DNA molecules are among the largest molecules known; they have molar masses of up to tens of billions of grams. On the other hand, RNA molecules vary greatly in size, some having a molar mass of about 25,000 g. Compared with proteins, which are made of up to 20 different amino acids, nucleic acids are fairly simple in composition. A DNA or RNA molecule contains only four types of building blocks: purines, pyrimidines, furanose sugars, and phosphate groups (Figure 22.15). Each purine or pyrimidine is called a *base*.

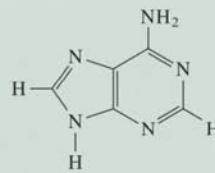
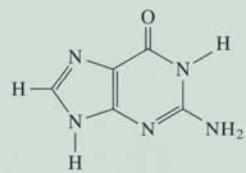
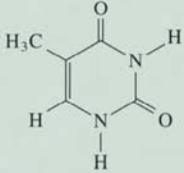
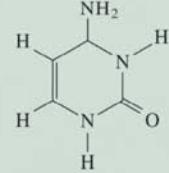
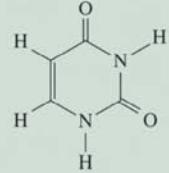
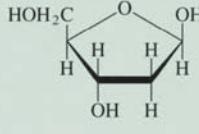
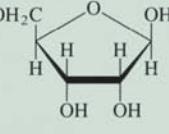
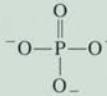
In the 1940s, the American biochemist Erwin Chargaff studied DNA molecules obtained from various sources and observed certain regularities. *Chargaff's rules*, as his findings are now known, describe these patterns:

1. The amount of adenine (a purine) is equal to that of thymine (a pyrimidine); that is,  $A = T$ , or  $A/T = 1$ .
2. The amount of cytosine (a pyrimidine) is equal to that of guanine (a purine); that is,  $C = G$ , or  $C/G = 1$ .
3. The total number of purine bases is equal to the total number of pyrimidine bases; that is,  $A + G = C + T$ .

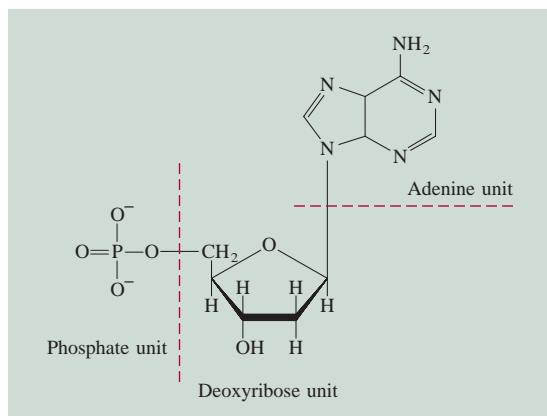
Based on chemical analyses and information obtained from X-ray diffraction measurements, the American biologist James Watson and the British biologist Francis Crick formulated the double-helical structure for the DNA molecule in 1953. Watson and Crick determined that the DNA molecule has two helical strands. Each strand is made up of **nucleotides**, which consist of a base, a deoxyribose, and a phosphate group linked together (Figure 22.16).

The key to the double-helical structure of DNA is the formation of hydrogen bonds between bases in the two strands of a molecule. Although hydrogen bonds can form between any two bases, called *base pairs*, Watson and Crick found that the most favorable couplings are between adenine and thymine and between cytosine and guanine (Figure 22.17). Note that this scheme is consistent with Chargaff's rules, because every purine base is hydrogen-bonded to a pyrimidine base, and vice versa ( $A + G = C + T$ ). Other attractive forces such as dipole-dipole interactions and van der Waals forces between the base pairs also help to stabilize the double helix.

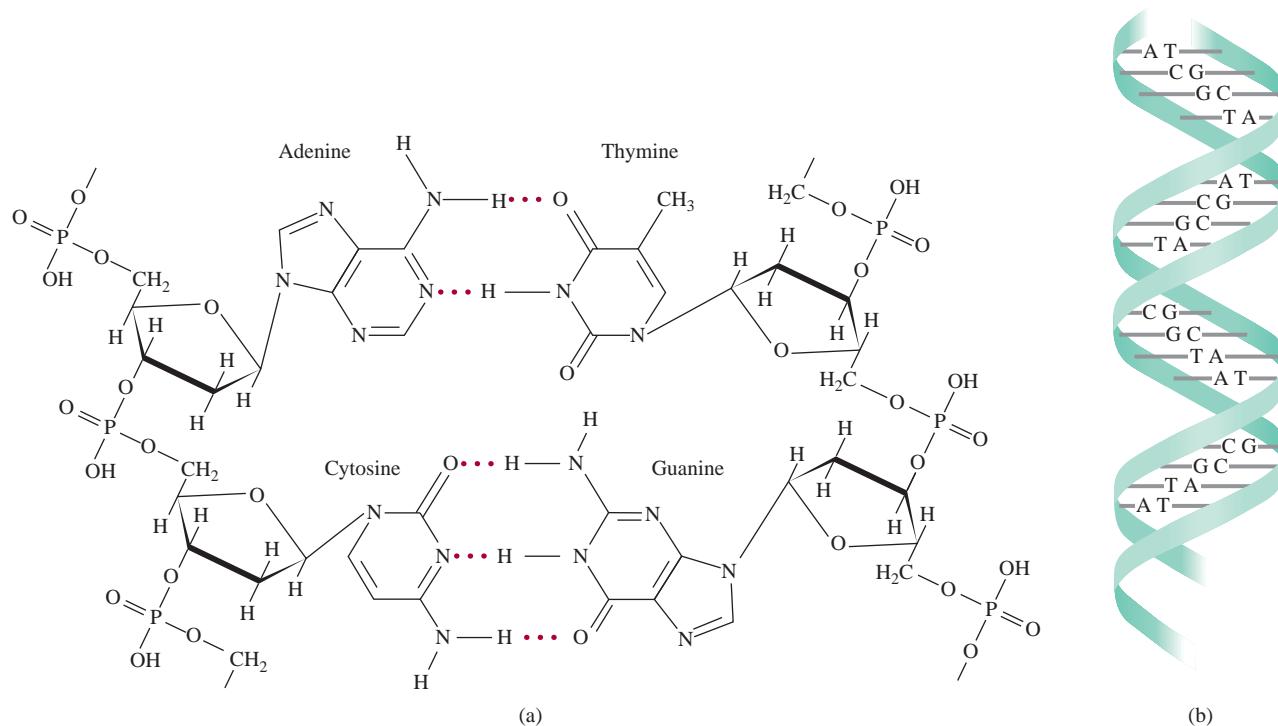
The structure of RNA differs from that of DNA in several respects. First, as shown in Figure 22.15, the four bases found in RNA molecules are adenine, cytosine, guanine, and uracil. Second, RNA contains the sugar ribose rather than the

|             | Found only in DNA   | Found in both DNA and RNA  | Found only in RNA   |
|-------------|---|--|---|
| Purines     |  |  |  |
| Pyrimidines |  |   |  |
| Sugars      |  |  |  |
| Phosphate   |   |  |   |

**Figure 22.15**  
The components of the nucleic acids DNA and RNA.



**Figure 22.16**  
Structure of a nucleotide, one of the repeating units in DNA.

**Figure 22.17**

(a) Base-pair formation by adenine and thymine and by cytosine and guanine. (b) The double-helical strand of a DNA molecule held together by hydrogen bonds (and other intermolecular forces) between base pairs A-T and C-G.

In the 1980s chemists discovered that certain RNAs can function as enzymes.

2-deoxyribose of DNA. Third, chemical analysis shows that the composition of RNA does not obey Chargaff's rules. In other words, the purine-to-pyrimidine ratio is not equal to 1 as in the case of DNA. This and other evidence rule out a double-helical structure. In fact, the RNA molecule exists as a single-strand polynucleotide. There are actually three types of RNA molecules—messenger RNA (*mRNA*), ribosomal RNA (*rRNA*), and transfer RNA (*tRNA*). These RNAs have similar nucleotides but differ from one another in molar mass, overall structure, and biological functions.

DNA and RNA molecules direct the synthesis of proteins in the cell, a subject that is beyond the scope of this book. Introductory texts in biochemistry and molecular biology explain this process.

## SUMMARY OF FACTS AND CONCEPTS

1. Polymers are large molecules made up of small, repeating units called monomers.
2. Proteins, nucleic acids, cellulose, and rubber are natural polymers. Nylon, Dacron, and Lucite are examples of synthetic polymers.
3. Organic polymers can be synthesized via addition reactions or condensation reactions.
4. Stereoisomers of a polymer made up of asymmetric monomers have different properties, depending on how the starting units are joined together.
5. Synthetic rubbers include polychloroprene and styrene-butadiene rubber, which is a copolymer of styrene and butadiene.

6. Structure determines the function and properties of proteins. To a great extent, hydrogen bonding and other intermolecular forces determine the structure of proteins.
7. The primary structure of a protein is its amino acid sequence. Secondary structure is the shape defined by hydrogen bonds joining the CO and NH groups of the amino acid backbone. Tertiary and quaternary structures are the three-dimensional folded arrangements of proteins that are stabilized by hydrogen bonds and other intermolecular forces.
8. Nucleic acids—DNA and RNA—are high-molar-mass polymers that carry genetic instructions for protein synthesis in cells. Nucleotides are the building blocks of DNA and RNA. DNA nucleotides each contain a purine or pyrimidine base, a deoxyribose molecule, and a phosphate group. RNA nucleotides are similar but contain different bases and ribose instead of deoxyribose.

## KEY WORDS

Amino acid, p. 745  
 Copolymer, p. 742  
 Denatured protein, p. 750

Deoxyribonucleic acid (DNA), p. 752  
 Homopolymer, p. 740

Monomer, p. 740  
 Nucleic acids, p. 752  
 Nucleotide, p. 752

Polymer, p. 740  
 Protein, p. 744  
 Ribonucleic acid (RNA), p. 752

## QUESTIONS AND PROBLEMS

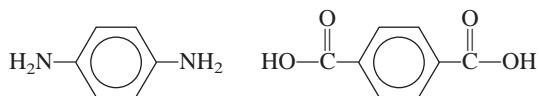
### Synthetic Organic Polymers

#### *Review Questions*

- 22.1 Define the following terms: monomer, polymer, homopolymer, copolymer.
- 22.2 Name 10 objects that contain synthetic organic polymers.
- 22.3 Calculate the molar mass of a particular polyethylene sample,  $\text{--CH}_2\text{--CH}_2\text{--}_n$ , where  $n = 4600$ .
- 22.4 Describe the two major mechanisms of organic polymer synthesis.
- 22.5 Discuss the three isomers of polypropene.
- 22.6 In Chapter 13 you learned about the colligative properties of solutions. Which of the colligative properties is suitable for determining the molar mass of a polymer? Why?

#### *Problems*

- 22.7 Teflon is formed by a radical addition reaction involving the monomer tetrafluoroethylene. Show the mechanism for this reaction.
- 22.8 Vinyl chloride,  $\text{H}_2\text{C}=\text{CHCl}$ , undergoes copolymerization with 1,1-dichloroethylene,  $\text{H}_2\text{C}=\text{CCl}_2$ , to form a polymer commercially known as Saran. Draw the structure of the polymer, showing the repeating monomer units.
- 22.9 Kevlar is a copolymer used in bullet-proof vests. It is formed in a condensation reaction between the following two monomers:



Sketch a portion of the polymer chain showing several monomer units. Write the overall equation for the condensation reaction.

- 22.10 Describe the formation of polystyrene.
- 22.11 Deduce plausible monomers for polymers with the following repeating units:
  - (a)  $\text{--CH}_2\text{--CF}_2\text{--}_n$
  - (b)  $\left( \text{CO--} \text{C}_6\text{H}_4\text{--CONH--} \text{C}_6\text{H}_4\text{--NH} \right)_n$
- 22.12 Deduce plausible monomers for polymers with the following repeating units:
  - (a)  $\text{--CH}_2\text{--CH=CH--CH}_2\text{--}_n$
  - (b)  $\text{--CO--} \text{--CH}_2\text{--}_6\text{NH--}_n$

### Proteins

#### *Review Questions*

- 22.13 Discuss the characteristics of an amide group and its importance in protein structure.
- 22.14 What is the  $\alpha$ -helical structure in proteins?
- 22.15 Describe the  $\beta$ -pleated structure present in some proteins.
- 22.16 Discuss the main functions of proteins in living systems.

- 22.17 Briefly explain the phenomenon of cooperativity exhibited by the hemoglobin molecule in binding oxygen.
- 22.18 Why is sickle-cell anemia called a molecular disease?

### Problems

- 22.19 Draw the structures of the dipeptides that can be formed from the reaction between the amino acids glycine and alanine.
- 22.20** Draw the structures of the dipeptides that can be formed from the reaction between the amino acids glycine and lysine.
- 22.21 The amino acid glycine can be condensed to form a polymer called polyglycine. Draw the repeating monomer unit.
- 22.22** The following are data obtained on the rate of product formation of an enzyme-catalyzed reaction:

| Temperature (°C) | Rate of Product Formation (M/s) |
|------------------|---------------------------------|
| 10               | 0.0025                          |
| 20               | 0.0048                          |
| 30               | 0.0090                          |
| 35               | 0.0086                          |
| 45               | 0.0012                          |

Comment on the dependence of rate on temperature. (No calculations are required.)

## Nucleic Acids

### Review Questions

- 22.23 Describe the structure of a nucleotide.
- 22.24 What is the difference between ribose and deoxyribose?
- 22.25 What are Chargaff's rules?
- 22.26 Describe the role of hydrogen bonding in maintaining the double-helical structure of DNA.

### Additional Problems

- 22.27 Discuss the importance of hydrogen bonding in biological systems. Use proteins and nucleic acids as examples.
- 22.28** Proteins vary widely in structure, whereas nucleic acids have rather uniform structures. How do you account for this major difference?
- 22.29 If untreated, fevers of 104°F or higher may lead to brain damage. Why?
- 22.30** The “melting point” of a DNA molecule is the temperature at which the double-helical strand breaks apart. Suppose you are given two DNA samples. One sample contains 45 percent C-G base pairs while the other contains 64 percent C-G base pairs. The total number of bases is the same in each sample. Which of the two samples has a higher melting point? Why?

- 22.31 When fruits such as apples and pears are cut, the exposed parts begin to turn brown. This is the result of an oxidation reaction catalyzed by enzymes present in the fruit. Often the browning action can be prevented or slowed by adding a few drops of lemon juice to the exposed areas. What is the chemical basis for this treatment?

- 22.32** “Dark meat” and “white meat” are one’s choices when eating a turkey. Explain what causes the meat to assume different colors. (*Hint:* The more active muscles in a turkey have a higher rate of metabolism and need more oxygen.)

- 22.33 Nylon can be destroyed easily by strong acids. Explain the chemical basis for the destruction. (*Hint:* The products are the starting materials of the polymerization reaction.)

- 22.34** Despite what you may have read in science fiction novels or seen in horror movies, it is extremely unlikely that insects can ever grow to human size. Why? (*Hint:* Insects do not have hemoglobin molecules in their blood.)

- 22.35 How many different tripeptides can be formed by lysine and alanine?

- 22.36** Chemical analysis shows that hemoglobin contains 0.34 percent Fe by mass. What is the minimum possible molar mass of hemoglobin? The actual molar mass of hemoglobin is four times this minimum value. What conclusion can you draw from these data?

- 22.37 The folding of a polypeptide chain depends not only on its amino acid sequence but also on the nature of the solvent. Discuss the types of interactions that might occur between water molecules and the amino acid residues of the polypeptide chain. Which groups would be exposed on the exterior of the protein in contact with water and which groups would be buried in the interior of the protein?

- 22.38** What kind of intermolecular forces are responsible for the aggregation of hemoglobin molecules that leads to sickle-cell anemia?

- 22.39 Draw structures of the nucleotides containing the following components: (a) deoxyribose and cytosine, (b) ribose and uracil.

- 22.40** When a nonapeptide (containing nine amino acid residues) isolated from rat brains was hydrolyzed, it gave the following smaller peptides as identifiable products: Gly-Ala-Phe, Ala-Leu-Val, Gly-Ala-Leu, Phe-Glu-His, and His-Gly-Ala. Reconstruct the amino acid sequence in the nonapeptide, giving your reasons. (Remember the convention for writing peptides.)

- 22.41 At neutral pH amino acids exist as dipolar ions. Using glycine as an example, and given that the  $pK_a$  of the carboxyl group is 2.3 and that of the ammonium group is 9.6, predict the predominant form of the molecule at pH 1, 7, and 12. Justify your answers using Equation (17.3).

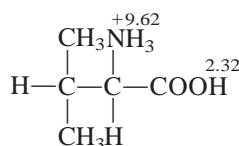
- 22.42** In Lewis Carroll's tale "Through the Looking Glass," Alice wonders whether "looking-glass milk" on the other side of the mirror would be fit to drink. Based on your knowledge of chirality and enzyme action, comment on the validity of Alice's concern.
- 22.43** The enthalpy change in the denaturation of a certain protein is 125 kJ/mol. If the entropy change is

397 J/K · mol, calculate the minimum temperature at which the protein would denature spontaneously.

- 22.44** When deoxyhemoglobin crystals are exposed to oxygen, they shatter. On the other hand, deoxymyoglobin crystals are unaffected by oxygen. Explain. (Myoglobin is made up of only one of the four sub-units, or polypeptide chains, in hemoglobin.)

## SPECIAL PROBLEMS

- 22.45** Nylon was designed to be a synthetic silk. (a) The average molar mass of a batch of nylon 66 is 12,000 g/mol. How many monomer units are there in this sample? (b) Which part of nylon's structure is similar to a polypeptide's structure? (c) How many different tripeptides (made up of three amino acids) can be formed from the amino acids alanine (Ala), glycine (Gly), and serine (Ser), which account for most of the amino acids in silk?
- 22.46** In protein synthesis, the selection of a particular amino acid is determined by the so-called genetic code, or a sequence of three bases in DNA. Will a sequence of only two bases unambiguously determine the selection of 20 amino acids found in proteins? Explain.
- 22.47** Consider the fully protonated amino acid valine:



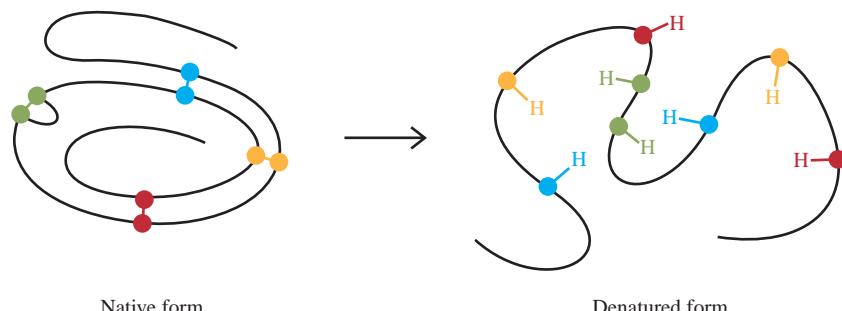
where the numbers denote the  $pK_a$  values. (a) Which of the two groups ( $-\text{NH}_3^+$  or  $-\text{COOH}$ ) is more acidic? (b) Calculate the predominant form of valine at pH 1.0, 7.0, and 12.0. (c) Calculate the isoelectric point of valine. (Hint: See Problem 17.109.)

- 22.48** Consider the formation of a dimeric protein



At 25°C, we have  $\Delta H^\circ = 17 \text{ kJ/mol}$  and  $\Delta S^\circ = 65 \text{ J/K} \cdot \text{mol}$ . Is the dimerization favored at this temperature? Comment on the effect of lowering the temperature. Does your result explain why some enzymes lose their activities under cold conditions?

- 22.49** The diagram (left) shows the structure of the enzyme ribonuclease in its native form. The three-dimensional protein structure is maintained in part by the disulfide bonds ( $-\text{S}-\text{S}-$ ) between the amino acid residues (each color sphere represents an S atom). Using certain denaturants, the compact structure is destroyed and the disulfide bonds are converted to sulphydryl groups ( $-\text{SH}$ ) shown on the right of the arrow. (a) Describe the bonding scheme in the disulfide bond in terms of hybridization. (b) Which amino acid in Table 22.2 contains the  $-\text{SH}$  group? (c) Predict the signs of  $\Delta H$  and  $\Delta S$  for the denaturation process. If denaturation is induced by a change in temperature, show why a rise in temperature would favor denaturation. (d) The sulphydryl groups can be oxidized (that is, removing the H atoms) to form the disulfide bonds. If the formation of the disulfide bonds is totally random between any two  $-\text{SH}$  groups, what is the fraction of the regenerated protein structures that corresponds to the native form? (e) An effective remedy to deodorize a dog that has been sprayed by a skunk is to rub the affected areas with a solution of an oxidizing agent such as hydrogen peroxide. What is the chemical basis for this action? (Hint: An odiferous component of a skunk's secretion is 2-butene-1-thiol,  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{SH}$ .)



## Units for the Gas Constant

In this appendix we will see how the gas constant  $R$  can be expressed in units  $\text{J/K} \cdot \text{mol}$ . Our first step is to derive a relationship between atm and pascal. We start with

$$\begin{aligned}\text{pressure} &= \frac{\text{force}}{\text{area}} \\ &= \frac{\text{mass} \times \text{acceleration}}{\text{area}} \\ &= \frac{\text{volume} \times \text{density} \times \text{acceleration}}{\text{area}} \\ &= \text{length} \times \text{density} \times \text{acceleration}\end{aligned}$$

By definition, the standard atmosphere is the pressure exerted by a column of mercury exactly 76 cm high of density 13.5951 g/cm<sup>3</sup>, in a place where acceleration due to gravity is 980.665 cm/s<sup>2</sup>. However, to express pressure in N/m<sup>2</sup> it is necessary to write

$$\begin{aligned}\text{density of mercury} &= 1.35951 \times 10^4 \text{ kg/m}^3 \\ \text{acceleration due to gravity} &= 9.80665 \text{ m/s}^2\end{aligned}$$

The standard atmosphere is given by

$$\begin{aligned}1 \text{ atm} &= (0.76 \text{ m Hg})(1.35951 \times 10^4 \text{ kg/m}^3)(9.80665 \text{ m/s}^2) \\ &= 101,325 \text{ kg m/m}^2 \cdot \text{s}^2 \\ &= 101,325 \text{ N/m}^2 \\ &= 101,325 \text{ Pa}\end{aligned}$$

From Section 5.4 we see that the gas constant  $R$  is given by  $0.082057 \text{ L} \cdot \text{atm/K} \cdot \text{mol}$ . Using the conversion factors

$$\begin{aligned}1 \text{ L} &= 1 \times 10^{-3} \text{ m}^3 \\ 1 \text{ atm} &= 101,325 \text{ N/m}^2\end{aligned}$$

we write

$$\begin{aligned}R &= \left( 0.082057 \frac{\text{L atm}}{\text{K mol}} \right) \left( \frac{1 \times 10^{-3} \text{ m}^3}{1 \text{ L}} \right) \left( \frac{101,325 \text{ N/m}^2}{1 \text{ atm}} \right) \\ &= 8.314 \frac{\text{N m}}{\text{K mol}} \\ &= 8.314 \frac{\text{J}}{\text{K mol}}\end{aligned}$$

$$\begin{aligned}1 \text{ L} \cdot \text{atm} &= (1 \times 10^{-3} \text{ m}^3)(101,325 \text{ N/m}^2) \\ &= 101.3 \text{ N m} \\ &= 101.3 \text{ J}\end{aligned}$$

and

# APPENDIX 2

## Selected Thermodynamic Data at 1 atm and 25°C\*

| Inorganic Substances                            |                             |                             |                       |
|---|-----------------------------|-----------------------------|-----------------------|
| Substance                                       | $\Delta H_f^\circ$ (kJ/mol) | $\Delta G_f^\circ$ (kJ/mol) | $S^\circ$ (J/K · mol) |
| Al( <i>s</i> )                                  | 0                           | 0                           | 28.3                  |
| Al <sup>3+</sup> ( <i>aq</i> )                  | -524.7                      | -481.2                      | -313.38               |
| Al <sub>2</sub> O <sub>3</sub> ( <i>s</i> )     | -1669.8                     | -1576.4                     | 50.99                 |
| Br <sub>2</sub> ( <i>l</i> )                    | 0                           | 0                           | 152.3                 |
| Br <sup>-</sup> ( <i>aq</i> )                   | -120.9                      | -102.8                      | 80.7                  |
| HBr( <i>g</i> )                                 | -36.2                       | -53.2                       | 198.48                |
| C(graphite)                                     | 0                           | 0                           | 5.69                  |
| C(diamond)                                      | 1.90                        | 2.87                        | 2.4                   |
| CO( <i>g</i> )                                  | -110.5                      | -137.3                      | 197.9                 |
| CO <sub>2</sub> ( <i>g</i> )                    | -393.5                      | -394.4                      | 213.6                 |
| CO <sub>2</sub> ( <i>aq</i> )                   | -412.9                      | -386.2                      | 121.3                 |
| CO <sub>3</sub> <sup>2-</sup> ( <i>aq</i> )     | -676.3                      | -528.1                      | -53.1                 |
| HCO <sub>3</sub> <sup>-</sup> ( <i>aq</i> )     | -691.1                      | -587.1                      | 94.98                 |
| H <sub>2</sub> CO <sub>3</sub> ( <i>aq</i> )    | -699.7                      | -623.2                      | 187.4                 |
| CS <sub>2</sub> ( <i>g</i> )                    | 115.3                       | 65.1                        | 237.8                 |
| CS <sub>2</sub> ( <i>l</i> )                    | 87.3                        | 63.6                        | 151.0                 |
| HCN( <i>aq</i> )                                | 105.4                       | 112.1                       | 128.9                 |
| CN <sup>-</sup> ( <i>aq</i> )                   | 151.0                       | 165.69                      | 117.99                |
| (NH <sub>2</sub> ) <sub>2</sub> CO( <i>s</i> )  | -333.19                     | -197.15                     | 104.6                 |
| (NH <sub>2</sub> ) <sub>2</sub> CO( <i>aq</i> ) | -319.2                      | -203.84                     | 173.85                |
| Ca( <i>s</i> )                                  | 0                           | 0                           | 41.6                  |
| Ca <sup>2+</sup> ( <i>aq</i> )                  | -542.96                     | -553.0                      | -55.2                 |
| CaO( <i>s</i> )                                 | -635.6                      | -604.2                      | 39.8                  |
| Ca(OH) <sub>2</sub> ( <i>s</i> )                | -986.6                      | -896.8                      | 76.2                  |
| CaF <sub>2</sub> ( <i>s</i> )                   | -1214.6                     | -1161.9                     | 68.87                 |
| CaCl <sub>2</sub> ( <i>s</i> )                  | -794.96                     | -750.19                     | 113.8                 |
| CaSO <sub>4</sub> ( <i>s</i> )                  | -1432.69                    | -1320.3                     | 106.69                |
| CaCO <sub>3</sub> ( <i>s</i> )                  | -1206.9                     | -1128.8                     | 92.9                  |
| Cl <sub>2</sub> ( <i>g</i> )                    | 0                           | 0                           | 223.0                 |
| Cl <sup>-</sup> ( <i>aq</i> )                   | -167.2                      | -131.2                      | 56.5                  |
| HCl( <i>g</i> )                                 | -92.3                       | -95.27                      | 187.0                 |

\*The  $\Delta H_f^\circ$ ,  $\Delta G_f^\circ$ , and  $S^\circ$  values for ions are based on the reference states  $\Delta H_f^\circ(\text{H}^+) = 0$ ,  $\Delta G_f^\circ(\text{H}^+) = 0$ , and  $S^\circ(\text{H}^+) = 0$ .

(Continued)

## Inorganic Substances—Cont.

| Substance                          | $\Delta H_f^\circ$ (kJ/mol) | $\Delta G_f^\circ$ (kJ/mol) | $S^\circ$ (J/K · mol) |
|------------------------------------|-----------------------------|-----------------------------|-----------------------|
| Cu(s)                              | 0                           | 0                           | 33.3                  |
| Cu <sup>+</sup> (aq)               | 51.88                       | 50.2                        | 40.6                  |
| Cu <sup>2+</sup> (aq)              | 64.39                       | 64.98                       | -99.6                 |
| CuO(s)                             | -155.2                      | -127.2                      | 43.5                  |
| Cu <sub>2</sub> O(s)               | -166.69                     | -146.36                     | 100.8                 |
| CuS(s)                             | -48.5                       | -49.0                       | 66.5                  |
| CuSO <sub>4</sub> (s)              | -769.86                     | -661.9                      | 113.39                |
| F <sub>2</sub> (g)                 | 0                           | 0                           | 203.34                |
| F <sup>-</sup> (aq)                | -329.1                      | -276.48                     | -9.6                  |
| HF(g)                              | -271.6                      | -270.7                      | 173.5                 |
| Fe(s)                              | 0                           | 0                           | 27.2                  |
| Fe <sup>2+</sup> (aq)              | -87.86                      | -84.9                       | -113.39               |
| Fe <sup>3+</sup> (aq)              | -47.7                       | -10.5                       | -293.3                |
| Fe <sub>2</sub> O <sub>3</sub> (s) | -822.2                      | -741.0                      | 90.0                  |
| Fe(OH) <sub>2</sub> (s)            | -568.19                     | -483.55                     | 79.5                  |
| Fe(OH) <sub>3</sub> (s)            | -824.25                     | ?                           | ?                     |
| H(g)                               | 218.2                       | 203.2                       | 114.6                 |
| H <sub>2</sub> (g)                 | 0                           | 0                           | 131.0                 |
| H <sup>+</sup> (aq)                | 0                           | 0                           | 0                     |
| OH <sup>-</sup> (aq)               | -229.94                     | -157.30                     | -10.5                 |
| H <sub>2</sub> O(g)                | -241.8                      | -228.6                      | 188.7                 |
| H <sub>2</sub> O(l)                | -285.8                      | -237.2                      | 69.9                  |
| H <sub>2</sub> O <sub>2</sub> (l)  | -187.6                      | -118.1                      | ?                     |
| I <sub>2</sub> (s)                 | 0                           | 0                           | 116.7                 |
| I <sup>-</sup> (aq)                | 55.9                        | 51.67                       | 109.37                |
| HI(g)                              | 25.9                        | 1.30                        | 206.3                 |
| K(s)                               | 0                           | 0                           | 63.6                  |
| K <sup>+</sup> (aq)                | -251.2                      | -282.28                     | 102.5                 |
| KOH(s)                             | -425.85                     | ?                           | ?                     |
| KCl(s)                             | -435.87                     | -408.3                      | 82.68                 |
| KClO <sub>3</sub> (s)              | -391.20                     | -289.9                      | 142.97                |
| KClO <sub>4</sub> (s)              | -433.46                     | -304.18                     | 151.0                 |
| KBr(s)                             | -392.17                     | -379.2                      | 96.4                  |
| KI(s)                              | -327.65                     | -322.29                     | 104.35                |
| KNO <sub>3</sub> (s)               | -492.7                      | -393.1                      | 132.9                 |
| Li(s)                              | 0                           | 0                           | 28.0                  |
| Li <sup>+</sup> (aq)               | -278.46                     | -293.8                      | 14.2                  |
| Li <sub>2</sub> O(s)               | -595.8                      | ?                           | ?                     |
| LiOH(s)                            | -487.2                      | -443.9                      | 50.2                  |

(Continued)

### Inorganic Substances—Cont.

| Substance  | $\Delta H_f^\circ$ (kJ/mol) | $\Delta G_f^\circ$ (kJ/mol) | $S^\circ$ (J/K · mol) |
|--|-----------------------------|-----------------------------|-----------------------|
| Mg(s)  | 0                           | 0                           | 32.5                  |
| Mg <sup>2+</sup> (aq)                            | -461.96                     | -456.0                      | -117.99               |
| MgO(s)   | -601.8                      | -569.6                      | 26.78                 |
| Mg(OH) <sub>2</sub> (s)                          | -924.66                     | -833.75                     | 63.1                  |
| MgCl <sub>2</sub> (s)                            | -641.8                      | -592.3                      | 89.5                  |
| MgSO <sub>4</sub> (s)                            | -1278.2                     | -1173.6                     | 91.6                  |
| MgCO <sub>3</sub> (s)                            | -1112.9                     | -1029.3                     | 65.69                 |
| <br>   |                             |                             |                       |
| N <sub>2</sub> (g)                               | 0                           | 0                           | 191.5                 |
| N <sub>3</sub> <sup>-</sup> (aq)                 | 245.18                      | ?                           | ?                     |
| NH <sub>3</sub> (g)                              | -46.3                       | -16.6                       | 193.0                 |
| NH <sub>4</sub> <sup>+</sup> (aq)                | -132.80                     | -79.5                       | 112.8                 |
| NH <sub>4</sub> Cl(s)                            | -315.39                     | -203.89                     | 94.56                 |
| NH <sub>3</sub> (aq)                             | -80.3                       | -263.76                     | 111.3                 |
| N <sub>2</sub> H <sub>4</sub> (l)                | 50.4                        | ?                           | ?                     |
| NO(g)  | 90.4                        | 86.7                        | 210.6                 |
| NO <sub>2</sub> (g)                              | 33.85                       | 51.8                        | 240.46                |
| N <sub>2</sub> O <sub>4</sub> (g)                | 9.66                        | 98.29                       | 304.3                 |
| N <sub>2</sub> O(g)                              | 81.56                       | 103.6                       | 219.99                |
| HNO <sub>3</sub> (aq)                            | -207.4                      | -111.3                      | 146.4                 |
| <br>   |                             |                             |                       |
| Na(s)  | 0                           | 0                           | 51.05                 |
| Na <sup>+</sup> (aq)                             | -239.66                     | -261.87                     | 60.25                 |
| Na <sub>2</sub> O(s)                             | -415.89                     | -376.56                     | 72.8                  |
| NaCl(s)  | -411.0                      | -384.0                      | 72.38                 |
| NaI(s)   | -288.0                      | ?                           | ?                     |
| Na <sub>2</sub> SO <sub>4</sub> (s)              | -1384.49                    | -1266.8                     | 149.49                |
| NaNO <sub>3</sub> (s)                            | -466.68                     | -365.89                     | 116.3                 |
| Na <sub>2</sub> CO <sub>3</sub> (s)              | -1130.9                     | -1047.67                    | 135.98                |
| NaHCO <sub>3</sub> (s)                           | -947.68                     | -851.86                     | 102.09                |
| <br>   |                             |                             |                       |
| O(g)   | 249.4                       | 230.1                       | 160.95                |
| O <sub>2</sub> (g)                               | 0                           | 0                           | 205.0                 |
| O <sub>3</sub> (aq)                              | -12.09                      | 16.3                        | 110.88                |
| O <sub>3</sub> (g)                               | 142.2                       | 163.4                       | 237.6                 |
| <br>   |                             |                             |                       |
| P(white)   | 0                           | 0                           | 44.0                  |
| P(red)   | -18.4                       | 13.8                        | 29.3                  |
| PO <sub>4</sub> <sup>3-</sup> (aq)               | -1284.07                    | -1025.59                    | -217.57               |
| P <sub>4</sub> O <sub>10</sub> (s)               | -3012.48                    | ?                           | ?                     |
| PH <sub>3</sub> (g)                              | 9.25                        | 18.2                        | 210.0                 |
| HPO <sub>4</sub> <sup>2-</sup> (aq)              | -1298.7                     | -1094.1                     | -35.98                |
| H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> (aq) | -1302.48                    | -1135.1                     | 89.1                  |

(Continued)

## Inorganic Substances—Cont.

| Substance                   | $\Delta H_f^\circ$ (kJ/mol) | $\Delta G_f^\circ$ (kJ/mol) | $S^\circ$ (J/K · mol) |
|-----------------------------|-----------------------------|-----------------------------|-----------------------|
| S(rhombic)                  | 0                           | 0                           | 31.88                 |
| S(monoclinic)               | 0.30                        | 0.10                        | 32.55                 |
| $\text{SO}_2(g)$            | −296.1                      | −300.4                      | 248.5                 |
| $\text{SO}_3(g)$            | −395.2                      | −370.4                      | 256.2                 |
| $\text{SO}_3^{2-}(aq)$      | −624.25                     | −497.06                     | 43.5                  |
| $\text{SO}_4^{2-}(aq)$      | −907.5                      | −741.99                     | 17.15                 |
| $\text{H}_2\text{S}(g)$     | −20.15                      | −33.0                       | 205.64                |
| $\text{HSO}_3^-(aq)$        | −627.98                     | −527.3                      | 132.38                |
| $\text{HSO}_4^-(aq)$        | −885.75                     | −752.87                     | 126.86                |
| $\text{H}_2\text{SO}_4(l)$  | −811.3                      | −690.0                      | 156.9                 |
| $\text{H}_2\text{SO}_4(aq)$ | −909.3                      | −744.5                      | 20.1                  |
| $\text{SF}_6(g)$            | −1096.2                     | −1105.3                     | 291.8                 |
| $\text{Zn}(s)$              | 0                           | 0                           | 41.6                  |
| $\text{Zn}^{2+}(aq)$        | −152.4                      | −147.2                      | −112.1                |
| $\text{ZnO}(s)$             | −348.0                      | −318.2                      | 43.9                  |
| $\text{ZnCl}_2(s)$          | −415.89                     | −369.26                     | 108.37                |
| $\text{ZnS}(s)$             | −202.9                      | −198.3                      | 57.7                  |
| $\text{ZnSO}_4(s)$          | −978.6                      | −871.6                      | 124.7                 |

## Organic Substances

| Substance                | Formula                                   | $\Delta H_f^\circ$ (kJ/mol) | $\Delta G_f^\circ$ (kJ/mol) | $S^\circ$ (J/K · mol) |
|--------------------------|---|-----------------------------|-----------------------------|-----------------------|
| Acetic acid( <i>l</i> )  | $\text{CH}_3\text{COOH}$                  | −484.2                      | −389.45                     | 159.8                 |
| Acetaldehyde( <i>g</i> ) | $\text{CH}_3\text{CHO}$                   | −166.35                     | −139.08                     | 264.2                 |
| Acetone( <i>l</i> )      | $\text{CH}_3\text{COCH}_3$                | −246.8                      | −153.55                     | 198.7                 |
| Acetylene( <i>g</i> )    | $\text{C}_2\text{H}_2$                    | 226.6                       | 209.2                       | 200.8                 |
| Benzene( <i>l</i> )      | $\text{C}_6\text{H}_6$                    | 49.04                       | 124.5                       | 172.8                 |
| Butane( <i>g</i> )       | $\text{C}_4\text{H}_{10}$                 | −124.7                      | −15.7                       | 310.0                 |
| Ethanol( <i>l</i> )      | $\text{C}_2\text{H}_5\text{OH}$           | −276.98                     | −174.18                     | 161.0                 |
| Ethane( <i>g</i> )       | $\text{C}_2\text{H}_6$                    | −84.7                       | −32.89                      | 229.5                 |
| Ethylene( <i>g</i> )     | $\text{C}_2\text{H}_4$                    | 52.3                        | 68.1                        | 219.5                 |
| Formic acid( <i>l</i> )  | $\text{HCOOH}$                            | −409.2                      | −346.0                      | 129.0                 |
| Glucose( <i>s</i> )      | $\text{C}_6\text{H}_{12}\text{O}_6$       | −1274.5                     | −910.56                     | 212.1                 |
| Methane( <i>g</i> )      | $\text{CH}_4$                             | −74.85                      | −50.8                       | 186.2                 |
| Methanol( <i>l</i> )     | $\text{CH}_3\text{OH}$                    | −238.7                      | −166.3                      | 126.8                 |
| Propane( <i>g</i> )      | $\text{C}_3\text{H}_8$                    | −103.9                      | −23.5                       | 269.9                 |
| Sucrose( <i>s</i> )      | $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ | −2221.7                     | −1544.3                     | 360.2                 |

# APPENDIX 3

## Mathematical Operations

### Logarithms

#### Common Logarithms

The concept of the logarithm is an extension of the concept of exponents, which is discussed in Chapter 1. The *common*, or base-10, logarithm of any number is the power to which 10 must be raised to equal the number. These examples illustrate this relationship:

| Logarithm           | Exponent         |
|---------------------|------------------|
| $\log 1 = 0$        | $10^0 = 1$       |
| $\log 10 = 1$       | $10^1 = 10$      |
| $\log 100 = 2$      | $10^2 = 100$     |
| $\log 10^{-1} = -1$ | $10^{-1} = 0.1$  |
| $\log 10^{-2} = -2$ | $10^{-2} = 0.01$ |

In each case, the logarithm of the number can be obtained by inspection.

Because the logarithms of numbers are exponents, they have the same properties as exponents. Thus, we have

| Logarithm                            | Exponent                       |
|--------------------------------------|--------------------------------|
| $\log AB = \log A + \log B$          | $10^A \times 10^B = 10^{A+B}$  |
| $\log \frac{A}{B} = \log A - \log B$ | $\frac{10^A}{10^B} = 10^{A-B}$ |

Furthermore,  $\log A^n = n \log A$ .

Now suppose we want to find the common logarithm of  $6.7 \times 10^{-4}$ . On most electronic calculators, the number is entered first and then the log key is pressed. This operation gives us

$$\log 6.7 \times 10^{-4} = -3.17$$

Note that there are as many digits *after* the decimal point as there are significant figures in the original number. The original number has two significant figures and the “17” in −3.17 tells us that the log has two significant figures. The 3 in 3.17 serves only to locate the decimal point in the number  $6.7 \times 10^{-4}$ . Other examples are

| Number               | Common Logarithm |
|----------------------|------------------|
| 62                   | 1.79             |
| 0.872                | −0.0595          |
| $1.0 \times 10^{-7}$ | −7.00            |

Sometimes (as in the case of pH calculations) it is necessary to obtain the number whose logarithm is known. This procedure is known as taking the antilogarithm; it is simply

the reverse of taking the logarithm of a number. Suppose in a certain calculation we have  $\text{pH} = 1.46$  and are asked to calculate  $[\text{H}^+]$ . From the definition of pH ( $\text{pH} = -\log [\text{H}^+]$ ) we can write

$$[\text{H}^+] = 10^{-1.46}$$

Many calculators have a key labeled  $\log^{-1}$  or INV log to obtain antilogs. Other calculators have a  $10^x$  or  $y^x$  key (in which  $x$  corresponds to  $-1.46$  in our example and  $y$  is 10 for base-10 logarithm). Therefore, we find that  $[\text{H}^+] = 0.035 \text{ M}$ .

## Natural Logarithms

Logarithms taken to the base  $e$  instead of 10 are known as natural logarithms (denoted by  $\ln$  or  $\log_e$ );  $e$  is equal to 2.7183. The relationship between common logarithms and natural logarithms is

$$\begin{array}{ll} \log 10 = 1 & 10^1 = 10 \\ \ln 10 = 2.303 & e^{2.303} = 10 \end{array}$$

Thus,

$$\ln x = 2.303 \log x$$

To find the natural logarithm of 2.27, say, we first enter the number on the electronic calculator and then press the  $\ln$  key to get

$$\ln 2.27 = 0.820$$

If no  $\ln$  key is provided, we can proceed as

$$\begin{aligned} 2.303 \log 2.27 &= 2.303 \times 0.356 \\ &= 0.820 \end{aligned}$$

Sometimes we may be given the natural logarithm and asked to find the number it represents. For example,

$$\ln x = 59.7$$

On many calculators, we simply enter the number and press the  $e$  key:

$$e^{59.7} = 8.5 \times 10^{25}$$

## The Quadratic Equation

A quadratic equation takes the form

$$ax^2 + bx + c = 0$$

If coefficients  $a$ ,  $b$ , and  $c$  are known, then  $x$  is given by

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Suppose we have this quadratic equation:

$$2x^2 + 5x - 12 = 0$$

Solving for  $x$ , we write

$$\begin{aligned}x &= \frac{-5 \pm \sqrt{(5)^2 - 4(2)(-12)}}{2(2)} \\&= \frac{-5 \pm \sqrt{25 + 96}}{4}\end{aligned}$$

Therefore,

$$x = \frac{-5 + 11}{4} = \frac{3}{2}$$

and

$$x = \frac{-5 - 11}{4} = -4$$

## The Elements and the Derivation of Their Names and Symbols\*

| Element   | Symbol | Atomic No. | Atomic Mass <sup>†</sup> | Date of Discovery | Discoverer and Nationality <sup>‡</sup>  | Derivation   |
|-----------|--------|------------|--------------------------|-------------------|--|--|
| Actinium  | Ac     | 89         | (227)                    | 1899              | A. Debierne (Fr.)  | Gr. <i>aktis</i> , beam or ray   |
| Aluminum  | Al     | 13         | 26.98                    | 1827              | F. Wochler (Ge.)   | Alum, the aluminum compound in which it was discovered; derived from L. <i>alumen</i> , astringent taste   |
| Americium | Am     | 95         | (243)                    | 1944              | A. Ghiorso (USA)<br>R. A. James (USA)<br>G. T. Seaborg (USA)<br>S. G. Thompson (USA) | The Americas   |
| Antimony  | Sb     | 51         | 121.8                    | Ancient           |  | L. <i>antimonium</i> ( <i>anti</i> , opposite of; <i>monium</i> , isolated condition), so named because it is a tangible (metallic) substance which combines readily; symbol, L. <i>stibium</i> , mark |
| Argon     | Ar     | 18         | 39.95                    | 1894              | Lord Raleigh (GB)<br>Sir William Ramsay (GB)   | Gr. <i>argos</i> , inactive  |
| Arsenic   | As     | 33         | 74.92                    | 1250              | Albertus Magnus (Ge.)  | Gr. <i>aksenikon</i> , yellow pigment; L. <i>arsenicum</i> , orpiment; the Greeks once used arsenic trisulfide as a pigment  |
| Astatine  | At     | 85         | (210)                    | 1940              | D. R. Corson (USA)<br>K. R. MacKenzie (USA)<br>E. Segre (USA)                        | Gr. <i>astatos</i> , unstable  |
| Barium    | Ba     | 56         | 137.3                    | 1808              | Sir Humphry Davy (GB)  | barite, a heavy spar, derived from Gr. <i>barys</i> , heavy  |
| Berkelium | Bk     | 97         | (247)                    | 1950              | G. T. Seaborg (USA)<br>S. G. Thompson (USA)<br>A. Ghiorso (USA)                      | Berkeley, Calif.   |

**Source:** From "The Elements and Derivation of Their Names and Symbols," G. P. Dinga, *Chemistry* 41 (2), 20–22 (1968). Copyright by the American Chemical Society.

\*At the time this table was drawn up, only 103 elements were known to exist.

<sup>†</sup>The atomic masses given here correspond to the 1961 values of the Commission on Atomic Weights. Masses in parentheses are those of the most stable or most common isotopes.

<sup>‡</sup>The abbreviations are (Ar.) Arabic; (Au.) Austrian; (Du.) Dutch; (Fr.) French; (Ge.) German; (GB) British; (Gr.) Greek; (H.) Hungarian; (I.) Italian; (L.) Latin; (P.) Polish; (R.) Russian; (Sp.) Spanish; (Swe.) Swedish; (USA) American.

| Element     | Symbol | Atomic No. | Atomic Mass | Date of Discovery | Discoverer and Nationality  | Derivation  |
|-------------|--------|------------|-------------|-------------------|---|---|
| Beryllium   | Be     | 4          | 9.012       | 1828              | F. Woehler (Ge.)<br>A. A. B. Bussy (Fr.)  | Fr. <i>beryl</i> , sweet  |
| Bismuth     | Bi     | 83         | 209.0       | 1753              | Claude Geoffroy (Fr.)   | Ge. <i>bismuth</i> , probably a distortion of <i>weisse masse</i> (white mass) in which it was found                            |
| Boron       | B      | 5          | 10.81       | 1808              | Sir Humphry Davy (GB)<br>J. L. Gay-Lussac (Fr.)<br>L. J. Thenard (Fr.)                  | The compound borax, derived from Ar. <i>buraq</i> , white   |
| Bromine     | Br     | 35         | 79.90       | 1826              | A. J. Balard (Fr.)  | Gr. <i>bromos</i> , stench  |
| Cadmium     | Cd     | 48         | 112.4       | 1817              | Fr. Stromeyer (Ge.)   | Gr. <i>kadmia</i> , earth;<br>L. <i>cadmia</i> , calamine (because it is found along with calamine)                             |
| Calcium     | Ca     | 20         | 40.08       | 1808              | Sir Humphry Davy (GB)   | L. <i>calx</i> , lime   |
| Californium | Cf     | 98         | (249)       | 1950              | G. T. Seaborg (USA)<br>S. G. Thompson (USA)<br>A. Ghiorso (USA)<br>K. Street, Jr. (USA) | California  |
| Carbon      | C      | 6          | 12.01       | Ancient           |   | L. <i>carbo</i> , charcoal  |
| Cerium      | Ce     | 58         | 140.1       | 1803              | J. J. Berzelius (Swe.)<br>William Hisinger (Swe.)<br>M. H. Klaproth (Ge.)               | Asteroid Ceres  |
| Cesium      | Cs     | 55         | 132.9       | 1860              | R. Bunsen (Ge.)<br>G. R. Kirchhoff (Ge.)  | L. <i>caesium</i> , blue (cesium was discovered by its spectral lines, which are blue)  |
| Chlorine    | Cl     | 17         | 35.45       | 1774              | K. W. Scheele (Swe.)  | Gr. <i>chloros</i> , light green  |
| Chromium    | Cr     | 24         | 52.00       | 1797              | L. N. Vauquelin (Fr.)   | Gr. <i>chroma</i> , color (because it is used in pigments)  |
| Cobalt      | Co     | 27         | 58.93       | 1735              | G. Brandt (Ge.)   | Ge. <i>Kobold</i> , goblin (because the ore yielded cobalt instead of the expected metal, copper, it was attributed to goblins) |
| Copper      | Cu     | 29         | 63.55       | Ancient           |   | L. <i>cuprum</i> , copper, derived from <i>cyprium</i> , Island of Cyprus, the main source of ancient copper                    |
| Curium      | Cm     | 96         | (247)       | 1944              | G. T. Seaborg (USA)<br>R. A. James (USA)<br>A. Ghiorso (USA)                            | Pierre and Marie Curie  |
| Dysprosium  | Dy     | 66         | 162.5       | 1886              | Lecoq de Boisbaudran (Fr.)  | Gr. <i>dysprositos</i> , hard to get at   |
| Einsteinium | Es     | 99         | (254)       | 1952              | A. Ghiorso (USA)  | Albert Einstein   |
| Erbium      | Er     | 68         | 167.3       | 1843              | C. G. Mosander (Swe.)   | Ytterby, Sweden, where many rare earths were discovered   |

(Continued)

| Element    | Symbol | Atomic No. | Atomic Mass | Date of Discovery | Discoverer and Nationality   | Derivation   |
|------------|--------|------------|-------------|-------------------|--|--|
| Europium   | Eu     | 63         | 152.0       | 1896              | E. Demarcay (Fr.)  | Europe   |
| Fermium    | Fm     | 100        | (253)       | 1953              | A. Ghiorso (USA)   | Enrico Fermi   |
| Fluorine   | F      | 9          | 19.00       | 1886              | H. Moissan (Fr.)   | Mineral fluorspar, from L. <i>fluere</i> , flow (because fluorspar was used as a flux)               |
| Francium   | Fr     | 87         | (223)       | 1939              | Marguerite Perey (Fr.)   | France   |
| Gadolinium | Gd     | 64         | 157.3       | 1880              | J. C. Marignac (Fr.)   | Johan Gadolin, Finnish rare earth chemist  |
| Gallium    | Ga     | 31         | 69.72       | 1875              | Lecoq de Boisbaudran (Fr.)   | L. <i>Gallia</i> , France  |
| Germanium  | Ge     | 32         | 72.59       | 1886              | Clemens Winkler (Ge.)  | L. <i>Germania</i> , Germany   |
| Gold       | Au     | 79         | 197.0       | Ancient           |  | L. <i>aurum</i> , shining dawn   |
| Hafnium    | Hf     | 72         | 178.5       | 1923              | D. Coster (Du.)<br>G. von Hevesey (H.)   | L. <i>Hafnia</i> , Copenhagen  |
| Helium     | He     | 2          | 4.003       | 1868              | P. Janssen (spectr) (Fr.)<br>Sir William Ramsay (isolated) (GB)                    | Gr. <i>helios</i> , sun (because it was first discovered in the sun's spectrum)                      |
| Holmium    | Ho     | 67         | 164.9       | 1879              | P. T. Cleve (Swe.)   | L. <i>Holmia</i> , Stockholm   |
| Hydrogen   | H      | 1          | 1.008       | 1766              | Sir Henry Cavendish (GB)   | Gr. <i>hydro</i> , water; <i>genes</i> , forming (because it produces water when burned with oxygen) |
| Indium     | In     | 49         | 114.8       | 1863              | F. Reich (Ge.)<br>T. Richter (Ge.)   | Indigo, because of its indigo blue lines in the spectrum   |
| Iodine     | I      | 53         | 126.9       | 1811              | B. Courtois (Fr.)  | Gr. <i>iodes</i> , violet  |
| Iridium    | Ir     | 77         | 192.2       | 1803              | S. Tennant (GB)  | L. <i>iris</i> , rainbow   |
| Iron       | Fe     | 26         | 55.85       | Ancient           |  | L. <i>ferrum</i> , iron  |
| Krypton    | Kr     | 36         | 83.80       | 1898              | Sir William Ramsay (GB)<br>M. W. Travers (GB)                                      | Gr. <i>kryptos</i> , hidden  |
| Lanthanum  | La     | 57         | 138.9       | 1839              | C. G. Mosander (Swe.)  | Gr. <i>lanthanein</i> , concealed  |
| Lawrencium | Lr     | 103        | (257)       | 1961              | A. Ghiorso (USA)<br>T. Sikkeland (USA)<br>A. E. Larsh (USA)<br>R. M. Latimer (USA) | E. O. Lawrence (USA), inventor of the cyclotron  |
| Lead       | Pb     | 82         | 207.2       | Ancient           |  | Symbol, L. <i>plumbum</i> , lead, meaning heavy  |
| Lithium    | Li     | 3          | 6.941       | 1817              | A. Arfvedson (Swe.)  | Gr. <i>lithos</i> , rock (because it occurs in rocks)  |
| Lutetium   | Lu     | 71         | 175.0       | 1907              | G. Urbain (Fr.)<br>C. A. von Welsbach (Au.)  | <i>Lutetia</i> , ancient name for Paris  |
| Magnesium  | Mg     | 12         | 24.31       | 1808              | Sir Humphry Davy (GB)  | <i>Magnesia</i> , a district in Thessaly; possibly derived from L. <i>magnesia</i>                   |
| Manganese  | Mn     | 25         | 54.94       | 1774              | J. G. Gahn (Swe.)  | L. <i>magnes</i> , magnet  |

(Continued)

| Element     | Symbol | Atomic No. | Atomic Mass | Date of Discovery | Discoverer and Nationality   | Derivation  |
|-------------|--------|------------|-------------|-------------------|--|---|
| Mendelevium | Md     | 101        | (256)       | 1955              | A. Ghiorso (USA)<br>G. R. Choppin (USA)<br>G. T. Seaborg (USA)<br>B. G. Harvey (USA)<br>S. G. Thompson (USA) | Mendeleev, Russian chemist who prepared the periodic chart and predicted properties of undiscovered elements  |
| Mercury     | Hg     | 80         | 200.6       | Ancient           |  | Symbol, L. <i>hydrargyrum</i> , liquid silver   |
| Molybdenum  | Mo     | 42         | 95.94       | 1778              | G. W. Scheele (Swe.)   | Gr. <i>molybdos</i> , lead  |
| Neodymium   | Nd     | 60         | 144.2       | 1885              | C. A. von Welsbach (Au.)   | Gr. <i>neos</i> , new; <i>didymos</i> , twin  |
| Neon        | Ne     | 10         | 20.18       | 1898              | Sir William Ramsay (GB)<br>M. W. Travers (GB)  | Gr. <i>neos</i> , new   |
| Neptunium   | Np     | 93         | (237)       | 1940              | E. M. McMillan (USA)<br>P. H. Abelson (USA)  | Planet Neptune  |
| Nickel      | Ni     | 28         | 58.69       | 1751              | A. F. Cronstedt (Swe.)   | Swe. <i>kopparnickel</i> , false copper; also Ge. <i>nickel</i> , referring to the devil that prevented copper from being extracted from nickel ores                          |
| Niobium     | Nb     | 41         | 92.91       | 1801              | Charles Hatchett (GB)  | Gr. <i>Niobe</i> , daughter of Tantalus (niobium was considered identical to tantalum, named after <i>Tantalus</i> , until 1884; originally called columbium, with symbol Cb) |
| Nitrogen    | N      | 7          | 14.01       | 1772              | Daniel Rutherford (GB)   | Fr. <i>nitrogene</i> , derived from L. <i>nitrum</i> , native soda, or Gr. <i>nitron</i> , native soda, and Gr. <i>genes</i> , forming  |
| Nobelium    | No     | 102        | (253)       | 1958              | A. Ghiorso (USA)<br>T. Sikkeland (USA)<br>J. R. Walton (USA)<br>G. T. Seaborg (USA)                          | Alfred Nobel  |
| Osmium      | Os     | 76         | 190.2       | 1803              | S. Tennant (GB)  | Gr. <i>osme</i> , odor  |
| Oxygen      | O      | 8          | 16.00       | 1774              | Joseph Priestley (GB)<br>C. W. Scheele (Swe.)  | Fr. <i>oxygene</i> , generator of acid, derived from Gr. <i>oxys</i> , acid, and L. <i>genes</i> , forming (because it was once thought to be a part of all acids)            |
| Palladium   | Pd     | 46         | 106.4       | 1803              | W. H. Wollaston (GB)   | Asteroid Pallas   |
| Phosphorus  | P      | 15         | 30.97       | 1669              | H. Brandt (Ge.)  | Gr. <i>phosphoros</i> , light bearing   |
| Platinum    | Pt     | 78         | 195.1       | 1735<br>1741      | A. de Ulloa (Sp.)<br>Charles Wood (GB)   | Sp. <i>platina</i> , silver   |

(Continued)

| Element      | Symbol | Atomic No. | Atomic Mass | Date of Discovery | Discoverer and Nationality   | Derivation   |
|--------------|--------|------------|-------------|-------------------|--|--|
| Plutonium    | Pu     | 94         | (242)       | 1940              | G. T. Seaborg (USA)<br>E. M. McMillan (USA)<br>J. W. Kennedy (USA)<br>A. C. Wahl (USA) | Planet Pluto   |
| Polonium     | Po     | 84         | (210)       | 1898              | Marie Curie (P.)   | Poland   |
| Potassium    | K      | 19         | 39.10       | 1807              | Sir Humphry Davy (GB)  | Symbol, L. <i>kalium</i> , potash  |
| Praseodymium | Pr     | 59         | 140.9       | 1885              | C. A. von Welsbach (Au.)   | Gr. <i>prasios</i> , green; <i>didymos</i> , twin  |
| Promethium   | Pm     | 61         | (147)       | 1945              | J. A. Marinsky (USA)<br>L. E. Glendenin (USA)<br>C. D. Coryell (USA)                   | Gr. mythology, <i>Prometheus</i> the Greek Titan who stole fire from heaven,                                     |
| Protactinium | Pa     | 91         | (231)       | 1917              | O. Hahn (Ge.)<br>L. Meitner (Au.)  | Gr. <i>protos</i> , first; <i>actinium</i> (because it disintegrates into actinium)                              |
| Radium       | Ra     | 88         | (226)       | 1898              | Pierre and Marie Curie (Fr.; P.)   | L. <i>radius</i> , ray   |
| Radon        | Rn     | 86         | (222)       | 1900              | F. E. Dorn (Ge.)   | Derived from radium with suffix "on" common to inert gases (once called nitron, meaning shining, with symbol Nt) |
| Rhenium      | Re     | 75         | 186.2       | 1925              | W. Noddack (Ge.)<br>I. Tacke (Ge.)<br>Otto Berg (Ge.)                                  | L. <i>Rhenus</i> , Rhine   |
| Rhodium      | Rh     | 45         | 102.9       | 1804              | W. H. Wollaston (GB)   | Gr. <i>rhodon</i> , rose (because some of its salts are rose-colored)  |
| Rubidium     | Rb     | 37         | 85.47       | 1861              | R. W. Bunsen (Ge.)<br>G. Kirchoff (Ge.)  | L. <i>rubidius</i> , dark red (discovered with the spectroscope, its spectrum shows red lines)                   |
| Ruthenium    | Ru     | 44         | 101.1       | 1844              | K. K. Klaus (R.)   | L. <i>Ruthenia</i> , Russia  |
| Samarium     | Sm     | 62         | 150.4       | 1879              | Lecoq de Boisbaudran (Fr.)   | Samarskite, after Samarski, a Russian engineer   |
| Scandium     | Sc     | 21         | 44.96       | 1879              | L. F. Nilson (Swe.)  | Scandinavia  |
| Selenium     | Se     | 34         | 78.96       | 1817              | J. J. Berzelius (Swe.)   | Gr. <i>selene</i> , moon (because it resembles tellurium, named for the earth)                                   |
| Silicon      | Si     | 14         | 28.09       | 1824              | J. J. Berzelius (Swe.)   | L. <i>silex</i> , <i>silicis</i> , flint   |
| Silver       | Ag     | 47         | 107.9       | Ancient           |  | Symbol, L. <i>argentum</i> , silver  |
| Sodium       | Na     | 11         | 22.99       | 1807              | Sir Humphry Davy (GB)  | L. <i>sodanum</i> , headache remedy; symbol, L. <i>natrium</i> , soda  |
| Strontium    | Sr     | 38         | 87.62       | 1808              | Sir Humphry Davy (GB)  | Strontian, Scotland, derived from mineral strontionite   |
| Sulfur       | S      | 16         | 32.07       | Ancient           |  | L. <i>sulphurium</i> (Sanskrit, <i>sulvere</i> )   |

(Continued)

| Element    | Symbol | Atomic No. | Atomic Mass | Date of Discovery | Discoverer and Nationality                    | Derivation  |
|------------|--------|------------|-------------|-------------------|---|---|
| Tantalum   | Ta     | 73         | 180.9       | 1802              | A. G. Ekeberg (Swe.)                          | Gr. mythology, <i>Tantalus</i> , because of difficulty in isolating it (Tantalus, son of Zeus, was punished by being forced to stand up to his chin in water that receded whenever he tried to drink) |
| Technetium | Tc     | 43         | (99)        | 1937              | C. Perrier (I.)                               | Gr. <i>technetos</i> , artificial (because it was the first artificial element)   |
| Tellurium  | Te     | 52         | 127.6       | 1782              | F. J. Müller (Au.)                            | L. <i>tellus</i> , earth  |
| Terbium    | Tb     | 65         | 158.9       | 1843              | C. G. Mosander (Swe.)                         | Ytterby, Sweden   |
| Thallium   | Tl     | 81         | 204.4       | 1861              | Sir William Crookes (GB)                      | Gr. <i>thallos</i> , a budding twig (because its spectrum shows a bright green line)  |
| Thorium    | Th     | 90         | 232.0       | 1828              | J. J. Berzelius (Swe.)                        | Mineral thorite, derived from <i>Thor</i> ; Norse god of war  |
| Thulium    | Tm     | 69         | 168.9       | 1879              | P. T. Cleve (Swe.)                            | <i>Thule</i> , early name for Scandinavia   |
| Tin        | Sn     | 50         | 118.7       | Ancient           |   | Symbol, L. <i>stannum</i> , tin   |
| Titanium   | Ti     | 22         | 47.88       | 1791              | W. Gregor (GB)                                | Gr. giants, the Titans, and L. <i>titans</i> , giant deities  |
| Tungsten   | W      | 74         | 183.9       | 1783              | J. J. and F. de Elhuyar (Sp.)                 | Swe. <i>tung sten</i> , heavy stone; symbol, wolframite, a mineral  |
| Uranium    | U      | 92         | 238.0       | 1789<br>1841      | M. H. Klaproth (Ge.)<br>E. M. Peligot (Fr.)   | Planet Uranus   |
| Vanadium   | V      | 23         | 50.94       | 1801<br>1830      | A. M. del Rio (Sp.)<br>N. G. Sefstrom (Swe.)  | <i>Vanadis</i> , Norse goddess of love and beauty   |
| Xenon      | Xe     | 54         | 131.3       | 1898              | Sir William Ramsay (GB)<br>M. W. Travers (GB) | Gr. <i>xenos</i> , stranger   |
| Ytterbium  | Yb     | 70         | 173.0       | 1907              | G. Urbain (Fr.)                               | Ytterby, Sweden   |
| Yttrium    | Y      | 39         | 88.91       | 1843              | C. G. Mosander (Swe.)                         | Ytterby, Sweden   |
| Zinc       | Zn     | 30         | 65.39       | 1746              | A. S. Marggraf (Ge.)                          | Ge. <i>zink</i> , of obscure origin   |
| Zirconium  | Zr     | 40         | 91.22       | 1789              | M. H. Klaproth (Ge.)                          | Zircon, in which it was found, derived from Ar. <i>zargum</i> , gold color  |

# GLOSSARY

The number in parentheses is the number of the section in which the term first appears.

## A

- absolute temperature scale.** A temperature scale on which absolute zero (0 K) is the lowest temperature (also called the Kelvin temperature scale). (5.3)
- absolute zero.** Theoretically the lowest attainable temperature. (5.3)
- accuracy.** The closeness of a measurement to the true value of the quantity that is being measured. (1.6)
- acid.** A substance that yields hydrogen ions ( $H^+$ ) when dissolved in water. (2.7)
- acid ionization constant ( $K_a$ ).** The equilibrium constant for acid ionization. (16.5)
- actinide series.** Elements that have incompletely filled  $5f$  subshells or readily give rise to cations that have incompletely filled  $5f$  subshells. (7.9)
- activated complex.** The species temporarily formed by reactant molecules as a result of a collision before they form the product. (14.4)
- activation energy.** The minimum amount of energy required to initiate a chemical reaction. (14.4)
- activity series.** A summary of the results of many possible displacement reactions. (4.4)
- actual yield.** The amount of product actually obtained in a reaction. (3.10)
- addition reaction.** A reaction in which one molecule is added to another. (11.2)
- adhesion.** Attraction between unlike molecules. (12.3)
- alcohol.** An organic compound containing the hydroxyl group ( $-OH$ ). (11.4)
- aldehydes.** Compounds with a carbonyl functional group and the general formula  $RCHO$ , in which R is an H atom, an alkyl, or an aromatic hydrocarbon group. (11.4)
- aliphatic hydrocarbons.** Hydrocarbons that do not contain the benzene group or the benzene ring. (11.1)
- alkali metals.** The Group 1A elements (Li, Na, K, Rb, Cs, and Fr). (2.4)
- alkaline earth metals.** The Group 2A elements (Be, Mg, Ca, Sr, Ba, and Ra). (2.4)
- alkanes.** Hydrocarbons having the general formula  $C_nH_{2n+2}$ , in which  $n = 1, 2, \dots$  (11.2)

**alkenes.** Hydrocarbons that contain one or more carbon-carbon double bonds. They have the general formula  $C_nH_{2n}$  in which  $n = 2, 3, \dots$  (11.2)

**alkynes.** Hydrocarbons that contain one or more carbon-carbon triple bonds. They have the general formula  $C_nH_{2n-2}$ , in which  $n = 2, 3, \dots$  (11.2)

**allotropes.** Two or more forms of the same element that differ significantly in chemical and physical properties. (2.6)

**alpha particles.** See alpha rays.

**alpha ( $\alpha$ ) rays.** Helium ions with a charge of +2. (2.2)

**amines.** Organic bases that have the functional group  $-NR_2$ , in which R may be H, an alkyl group, or an aromatic hydrocarbon group. (11.4)

**amino acid.** A special kind of carboxylic acid that contains at least one carboxyl group ( $-COOH$ ) and at least one amino group ( $-NH_2$ ). (22.3)

**amorphous solid.** A solid that lacks a regular three-dimensional arrangement of atoms or molecules. (12.5)

**amphoteric oxide.** An oxide that exhibits both acidic and basic properties. (8.6)

**amplitude.** The vertical distance from the middle of a wave to the peak or trough. (7.1)

**anion.** An ion with a net negative charge. (2.5)

**anode.** The electrode at which oxidation occurs. (19.2)

**antibonding molecular orbital.** A molecular orbital that is of higher energy and lower stability than the atomic orbitals from which it was formed. (10.6)

**aqueous solution.** A solution in which the solvent is water. (4.1)

**aromatic hydrocarbon.** A hydrocarbon that contains one or more benzene rings. (11.1)

**atmospheric pressure.** The pressure exerted by Earth's atmosphere. (5.2)

**atom.** The basic unit of an element that can enter into chemical combination. (2.2)

**atomic mass.** The mass of an atom in atomic mass units. (3.1)

**atomic mass unit (amu).** A mass exactly equal to one-twelfth the mass of one carbon-12 atom. (3.1)

**atomic number (Z).** The number of protons in the nucleus of an atom. (2.3)

**atomic orbital.** The wave function of an electron in an atom. (7.5)

**atomic radius.** One-half the distance between the nuclei in two adjacent atoms of the same element in a metal. For elements that exist as diatomic units, the atomic radius is one-half the distance between the nuclei of two atoms in a particular molecule. (8.3)

**Aufbau principle.** As protons are added one by one to the nucleus to build up the elements, electrons similarly are added to the atomic orbitals. (7.9)

**Avogadro's law.** At constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of the gas present. (5.3)

**Avogadro's number ( $N_A$ ).**  $6.022 \times 10^{23}$ ; the number of particles in a mole. (3.2)

## B

**barometer.** An instrument that measures atmospheric pressure. (5.2)

**base.** A substance that yields hydroxide ions ( $OH^-$ ) when dissolved in water. (2.7)

**base ionization constant ( $K_b$ ).** The equilibrium constant for the ionization of a base. (16.6)

**battery.** A galvanic cell or a series of several connected galvanic cells that can be used as a source of direct electric current at a constant voltage. (19.6)

**beta particles.** See beta rays.

**beta ( $\beta$ ) rays.** Streams of electrons emitted during the decay of certain radioactive substances. (2.2)

**bimolecular reaction.** An elementary step involving two molecules that is part of a reaction mechanism. (14.5)

**binary compounds.** Compounds containing just two elements. (2.7)

**boiling point.** The temperature at which the vapor pressure of a liquid is equal to the external atmospheric pressure. (12.6)

**bond enthalpy.** The enthalpy change required to break a bond in a mole of gaseous molecules. (9.10)

**bond length.** The distance between the centers of two bonded atoms in a molecule. (9.4)

**bond order.** The difference between the number of electrons in bonding molecular orbitals and antibonding molecular orbitals, divided by two. (10.6)

**bonding molecular orbital.** A molecular orbital that is of lower energy and greater stability than the atomic orbitals from which it was formed. (10.6)

**Born-Haber cycle.** The cycle that relates lattice energies of ionic compounds to ionization energies, electron affinities, and other atomic and molecular properties. (9.3)

**boundary surface diagram.** Diagram of the region containing about 90 percent of the electron density in an atomic orbital. (7.7)

**Boyle's law.** The volume of a fixed amount of gas is inversely proportional to the gas pressure at constant temperature. (5.3)

**breeder reactor.** A nuclear reactor that produces more fissionable material than it uses. (21.5)

**Brønsted acid.** A substance capable of donating a proton in a reaction. (4.3)

**Brønsted base.** A substance capable of accepting a proton in a reaction. (4.3)

**buffer solution.** A solution of (a) a weak acid or base and (b) its salt; both components must be present. A buffer solution has the ability to resist changes in pH when small amounts of either acid or base are added to it. (17.2)

## C

**calorimetry.** The measurement of heat changes. (6.5)

**carboxylic acids.** Acids that contain the carboxyl group ( $\text{—COOH}$ ). (11.4)

**catalyst.** A substance that increases the rate of a chemical reaction by providing an alternate reaction pathway without being consumed during the reaction. (14.6)

**cathode.** The electrode at which reduction occurs. (19.2)

**cation.** An ion with a net positive charge. (2.5)

**cell voltage.** Difference in electrical potential between the anode and the cathode of a galvanic cell. (19.2)

**Charles's and Gay-Lussac's law.** See Charles's law.

**Charles's law.** The volume of a fixed amount of gas is directly proportional to the absolute temperature of the gas when the pressure is held constant. (5.3)

**chelating agent.** A substance that forms complex ions with metal ions in solution. (20.2)

**chemical energy.** Energy stored within the structural units of chemical substances. (6.1)

**chemical equation.** An equation that uses chemical symbols to show what happens during a chemical reaction. (3.7)

**chemical equilibrium.** A state in which the rates of the forward and reverse reactions are equal and no net changes can be observed. (4.1, 15.1)

**chemical formula.** An expression showing the chemical composition of a compound

in terms of the symbols for the atoms of the elements involved. (2.6)

**chemical kinetics.** The area of chemistry concerned with the speeds, or rates, at which chemical reactions occur. (14.1)

**chemical property.** Any property of a substance that cannot be studied without converting the substance into some other substance. (1.4)

**chemical reaction.** Chemical change. (3.7)

**chemistry.** The science that studies the properties of substances and how substances react with one another. (1.3)

**chiral.** Compounds or ions that are not superimposable with their mirror images. (11.5)

**closed system.** A system that allows the exchange of energy (usually in the form of heat) but not mass with its surroundings. (6.2)

**cohesion.** The intermolecular attraction between like molecules. (12.3)

**colligative properties.** Properties of solutions that depend on the number of solute particles in solution and not on the nature of the solute. (13.6)

**combination reaction.** A reaction in which two or more substances combine to form a single product. (4.4)

**combustion reaction.** A reaction in which a substance reacts with oxygen, usually with the release of heat and light to produce a flame. (4.4)

**complex ion.** An ion containing a central metal cation bonded to one or more molecules or ions. (17.7)

**compound.** A substance composed of two or more elements chemically united in fixed proportions. (1.3)

**concentration of a solution.** The amount of solute present in a given quantity of solution. (4.5)

**condensation.** The phenomenon of going from the gaseous state to the liquid state. (12.6)

**condensation reaction.** The joining of two molecules and the elimination of a small molecule, usually water. (11.4)

**conformations.** Different spatial arrangements of a molecule that are generated by rotation about single bonds. (11.2)

**conjugate acid-base pair.** An acid and its conjugate base or a base and its conjugate acid. (16.1)

**coordinate covalent bond.** A bond in which the pair of electrons is supplied by one of the two bonded atoms. (9.9)

**coordination compound.** A neutral species containing a complex ion. (20.2)

**coordination number.** In a crystal lattice it is defined as the number of atoms (or ions) surrounding an atom (or ion) (12.4). In coordination compounds it is defined as the number of donor atoms surrounding the central metal atom in a complex. (20.2)

**copolymer.** A polymer containing two or more different monomers. (22.2)

**corrosion.** The deterioration of metals by an electrochemical process. (19.7)

**Coulomb's law.** The potential energy between two ions is directly proportional to the product of their charges and inversely proportional to the distance between them. (9.3)

**covalent bond.** A bond in which two electrons are shared by two atoms. (9.4)

**covalent compounds.** Compounds containing only covalent bonds. (9.4)

**critical mass.** The minimum mass of fissionable material required to generate a self-sustaining nuclear chain reaction. (21.5)

**critical pressure ( $P_c$ ).** The minimum pressure necessary to bring about liquefaction at the critical temperature. (12.6)

**critical temperature ( $T_c$ ).** The temperature above which a gas will not liquefy. (12.6)

**crystal-field splitting.** The energy difference between two sets of  $d$  orbitals of a metal atom in the presence of ligands. (20.4)

**crystalline solid.** A solid that possesses rigid and long-range structural order; its atoms, molecules, or ions occupy specific positions. (12.4)

**crystallization.** The process in which dissolved solute comes out of solution and forms crystals. (13.1)

**cycloalkanes.** Hydrocarbons having the general formula  $\text{C}_n\text{H}_{2n}$  in which  $n = 3, 4, \dots$  (11.2)

## D

**Dalton's law of partial pressures.** The total pressure of a mixture of gases is just the sum of the pressures that each gas would exert if it were present alone. (5.5)

**decomposition reaction.** The breakdown of a compound into two or more components. (4.4)

**delocalized molecular orbital.** A molecular orbital that is not confined between two adjacent bonding atoms but actually extends over three or more atoms. (11.3)

**denatured protein.** Protein that does not exhibit normal biological activities. (22.3)

**density.** The mass of a substance divided by its volume. (1.5)

**deoxyribonucleic acid (DNA).** A type of nucleic acid. (22.4)

**deposition.** The process in which vapor molecules are converted directly to the solid phase. (12.6)

**diagonal relationship.** Similarities between pairs of elements in different groups and periods of the periodic table. (8.6)

**diamagnetic.** Repelled by a magnet; a diamagnetic substance contains only paired electrons. (7.8)

**diatomic molecule.** A molecule that consists of two atoms. (2.5)

**diffusion.** The gradual mixing of molecules of one gas with the molecules of another by virtue of their kinetic properties. (5.6)

**dilution.** A procedure for preparing a less concentrated solution from a more concentrated solution. (4.5)

**dipole moment.** The product of charge and the distance between the charges in a molecule. (10.2)

**dipole-dipole forces.** Forces that act between polar molecules. (12.2)

**diprotic acid.** Each unit of the acid yields two hydrogen ions. (4.3)

**dispersion forces.** The attractive forces that arise as a result of temporary dipoles induced in the atoms or molecules. (12.2)

**displacement reaction.** A reaction in which an atom or an ion in a compound is replaced by an atom of another element. (4.4)

**donor atom.** The atom in a ligand that is bonded directly to the metal atom. (20.2)

**double bond.** A covalent bond in which two atoms share two pairs of electrons. (9.4)

**dynamic equilibrium.** The condition in which the rate of a forward process is exactly balanced by the rate of the reverse process. (12.6)

## E

**effusion.** The process by which a gas under pressure escapes from one compartment of a container to another by passing through a small opening. (5.6)

**electrochemistry.** The branch of chemistry that deals with the interconversion of electrical energy and chemical energy. (19.1)

**electrolysis.** A process in which electrical energy is used to bring about a nonspontaneous chemical reaction. (19.8)

**electrolyte.** A substance that, when dissolved in water, results in a solution that can conduct electricity. (4.1)

**electrolytic cell.** An apparatus for carrying out electrolysis. (19.8)

**electromagnetic radiation.** The emission and transmission of energy in the form of electromagnetic waves. (7.1)

**electromagnetic wave.** A wave that has an electric field component and a mutually perpendicular magnetic field component. (7.1)

**electromotive force (emf) ( $E$ ).** The voltage difference between electrodes. (19.2)

**electron.** A subatomic particle that has a very low mass and carries a single negative electric charge. (2.2)

**electron affinity.** The negative of the energy change that takes place when an electron is accepted by an atom (or an ion) in the gaseous state. (8.5)

**electron configuration.** The distribution of electrons among the various orbitals in an atom or molecule. (7.8)

**electron density.** The probability that an electron will be found at a particular region in an atomic orbital. (7.5)

**electronegativity.** The ability of an atom to attract electrons toward itself in a chemical bond. (9.5)

**element.** A substance that cannot be separated into simpler substances by chemical means. (1.3)

**elementary steps.** A series of simple reactions that represent the overall progress of a reaction at the molecular level. (14.5)

**emission spectrum.** The continuous or line spectrum of electromagnetic radiation emitted by a substance. (7.3)

**empirical formula.** An expression using chemical symbols to show the types of elements in a substance and the simplest ratios of the different kinds of atoms. (2.6)

**enantiomers.** Compounds and their nonsuperimposable mirror images. (11.5)

**end point.** Occurs in a titration when the indicator changes color. (17.4)

**endothermic processes.** Processes that absorb heat from the surroundings. (6.2)

**energy.** The capacity to do work or to produce change. (6.1)

**enthalpy ( $H$ ).** A thermodynamic quantity used to describe heat changes taking place at constant pressure. (6.4)

**enthalpy of reaction ( $\Delta H$ ).** The difference between the enthalpies of the products and the enthalpies of the reactants. (6.4)

**entropy ( $S$ ).** A measure of how spread out or dispersed the energy of a system is among the different possible ways that the system can contain energy. (18.3)

**enzyme.** A biological catalyst. (14.6)

**equilibrium constant.** A number equal to the ratio of the equilibrium concentrations of products to the equilibrium concentrations of reactants, each raised to the power of its stoichiometric coefficient. (15.1)

**equilibrium vapor pressure.** The vapor pressure measured for a dynamic equilibrium of condensation and evaporation. (12.6)

**equivalence point.** The point at which an acid is completely reacted with or neutralized by a base. (4.6)

**esters.** Compounds that have the general formula  $RCOOR'$ , in which R can be H or an alkyl group or an aromatic hydrocarbon group and R' is an alkyl group or an aromatic hydrocarbon group. (11.4)

**ether.** An organic compound containing the  $R—O—R'$  linkage, in which R and R' are alkyl and/or aromatic hydrocarbon groups. (11.4)

**evaporation.** The escape of molecules from the surface of a liquid; also called vaporization. (12.6)

**excess reagent.** A reactant present in a quantity greater than necessary to react

with the amount of the limiting reagent present. (3.9)

**excited level (or state).** A state that has higher energy than the ground state of the system. (7.3)

**exothermic processes.** Processes that give off heat to the surroundings. (6.2)

**extensive property.** A property that depends on how much matter is being considered. (1.4)

## F

**family.** The elements in a vertical column of the periodic table. (2.4)

**Faraday constant ( $F$ ).** Charge contained in 1 mole of electrons, equivalent to 96,485 coulombs. (19.4)

**first law of thermodynamics.** Energy can be converted from one form to another, but cannot be created or destroyed. (6.3)

**first-order reaction.** A reaction whose rate depends on reactant concentration raised to the first power. (14.3)

**formal charge.** The electrical charge difference between the number of valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure. (9.7)

**formation constant ( $K_f$ ).** The equilibrium constant for the complex ion formation. (17.7)

**free energy ( $G$ ).** The energy available to do useful work. (18.5)

**frequency ( $v$ ).** The number of waves that pass through a particular point per unit time. (7.1)

**fuel cell.** A galvanic cell that requires a continuous supply of reactants to keep functioning. (19.6)

**functional group.** That part of a molecule characterized by a special arrangement of atoms that is largely responsible for the chemical behavior of the parent molecule. (11.1)

## G

**galvanic cell.** An electrochemical cell that generates electricity by means of a spontaneous redox reaction. (19.2)

**gamma ( $\gamma$ ) rays.** High-energy radiation. (2.2)

**gas constant ( $R$ ).** The constant that appears in the ideal gas equation ( $PV = nRT$ ). It is expressed as  $0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol}$ , or  $8.314 \text{ J/K} \cdot \text{mol}$ . (5.4)

**geometric isomers.** Compounds with the same type and number of atoms and the same chemical bonds but different spatial arrangements; such isomers cannot be interconverted without breaking a chemical bond. (11.2)

**Gibbs free energy.** See free energy.

**Graham's law of diffusion.** Under the same conditions of temperature and pressure,

the rates of diffusion of gases are inversely proportional to the square roots of their molar masses. (5.6)

**gravimetric analysis.** An experimental procedure that involves the measurement of mass to identify an unknown component of a substance. (4.6)

**ground level (or state).** The lowest energy state of a system. (7.3)

**group.** The elements in a vertical column of the periodic table. (2.4)

## H

**half-cell reactions.** Oxidation and reduction reactions that occur at the electrodes. (19.2)

**half-life.** The time required for the concentration of a reactant to decrease to half its initial concentration. (14.3)

**half-reaction.** A reaction that explicitly shows electrons involved in either oxidation or reduction. (4.4)

**halogens.** The nonmetallic elements in Group 7A (F, Cl, Br, I, and At). (2.4)

**heat.** Transfer of energy between two bodies that are at different temperatures. (6.2)

**heat capacity (*C*).** The amount of heat required to raise the temperature of a given quantity of a substance by one degree Celsius. (6.5)

**Heisenberg uncertainty principle.** It is impossible to know simultaneously both the momentum and the position of a particle with certainty. (7.5)

**Henry's law.** The solubility of a gas in a liquid is proportional to the pressure of the gas over the solution. (13.5)

**Hess's law.** When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps. (6.6)

**heterogeneous equilibrium.** An equilibrium state in which the reacting species are not all in the same phase. (15.2)

**heterogeneous mixture.** The individual components of such a mixture remain physically separate and can be seen as separate components. (1.3)

**homogeneous equilibrium.** An equilibrium condition in which all reacting species are in the same phase. (15.2)

**homogeneous mixture.** The composition of the mixture is the same throughout the solution. (1.3)

**homonuclear diatomic molecule.** A diatomic molecule containing atoms of the same element. (10.6)

**homopolymer.** A polymer that is made from only one type of monomer. (22.2)

**Hund's rule.** The most stable arrangement of electrons in atomic subshells is the one with the greatest number of parallel spins. (7.8)

**hybrid orbitals.** Atomic orbitals obtained when two or more nonequivalent orbitals

of the same atom combine before covalent bond formation. (10.4)

**hybridization.** The process of mixing the atomic orbitals in an atom (usually the central atom) to generate a set of new atomic orbitals before covalent bond formation. (10.4)

**hydrates.** Compounds that have a specific number of water molecules attached to them. (2.7)

**hydration.** A process in which an ion or a molecule is surrounded by water molecules arranged in a specific manner. (4.1)

**hydrocarbons.** Compounds made up of only carbon and hydrogen. (11.1)

**hydrogen bond.** A special type of dipole-dipole interaction between the hydrogen atom bonded to an atom of a very electronegative element (F, N, O) and another atom of one of the three electronegative elements. (12.2)

**hydrogenation.** The addition of hydrogen, especially to compounds with double and triple carbon-carbon bonds. (11.2)

**hydronium ion.**  $\text{H}_3\text{O}^+$ . (4.3)

**hypothesis.** A tentative explanation for a set of observations. (1.2)

## I

**ideal gas.** A hypothetical gas whose pressure-volume-temperature behavior can be completely accounted for by the ideal gas equation. (5.4)

**ideal gas equation.** An equation expressing the relationships among pressure, volume, temperature, and amount of gas ( $PV = nRT$ , in which  $R$  is the gas constant). (5.4)

**ideal solution.** Any solution that obeys Raoult's law. (13.6)

**indicators.** Substances that have distinctly different colors in acidic and basic media. (4.6)

**induced dipole.** The separation of positive and negative charges in an atom (or a nonpolar molecule) caused by the proximity of an ion or a polar molecule. (12.2)

**inert complex.** A complex ion that undergoes very slow ligand exchange reactions. (20.5)

**intensive property.** A property that does not depend on how much matter is being considered. (1.4)

**intermediate.** A species that appears in the mechanism of the reaction (that is, in the elementary steps) but not in the overall balanced equation. (14.5)

**intermolecular forces.** Attractive forces that exist among molecules. (12.2)

**International System of Units.** A revised metric system (abbreviated SI) that is widely used in scientific research. (1.5)

**intramolecular forces.** Forces that hold atoms together in a molecule. (12.2)

**ion.** An atom or group of atoms that has a net positive or negative charge. (2.5)

**ion pair.** A species made up of at least one cation and at least one anion held together by electrostatic forces. (13.6)

**ion-dipole forces.** Forces that operate between an ion and a dipole. (12.2)

**ionic bond.** The electrostatic force that holds ions together in an ionic compound. (9.2)

**ionic compound.** Any neutral compound containing cations and anions. (2.5)

**ionic equation.** An equation that shows dissolved ionic compounds in terms of their free ions. (4.2)

**ionic radius.** The radius of a cation or an anion as measured in an ionic compound. (8.3)

**ionization energy.** The minimum energy required to remove an electron from an isolated atom (or an ion) in its ground state. (8.4)

**ion-product constant.** Product of hydrogen ion concentration and hydroxide ion concentration (both in molarity) at a particular temperature. (16.2)

**isoelectronic.** Ions, or atoms and ions, that possess the same number of electrons, and hence the same ground-state electron configuration, are said to be isoelectronic. (8.2)

**isolated system.** A system that does not allow the transfer of either mass or energy to or from its surroundings. (6.2)

**isotopes.** Atoms having the same atomic number but different mass numbers. (2.3)

## J

**Joule.** Unit of energy given by newtons × meters. (5.6)

## K

**Kelvin temperature scale.** See absolute temperature scale.

**ketones.** Compounds with a carbonyl functional group and the general formula  $\text{RR}'\text{CO}$ , in which R and R' are alkyl and/or aromatic hydrocarbon groups. (11.4)

**kinetic energy (KE).** Energy available because of the motion of an object. (5.6)

**kinetic molecular theory of gases.** A theory that describes the physical behavior of gases at the molecular level. (5.6)

## L

**labile complex.** Complexes that undergo rapid ligand exchange reactions. (20.5)

**lanthanide series.** Elements that have incompletely filled 4f subshells or readily give rise to cations that have incompletely filled 4f subshells. (7.9)

**lattice energy.** The energy required to completely separate one mole of a solid ionic compound into gaseous ions. (9.3)

**lattice points.** The positions occupied by atoms, molecules, or ions that define the geometry of a unit cell. (12.4)

**law.** A concise verbal or mathematical statement of a relationship between phenomena that is always the same under the same conditions. (1.2)

**law of conservation of energy.** The total quantity of energy in the universe is constant. (6.1)

**law of conservation of mass.** Matter can be neither created nor destroyed. (2.1)

**law of definite proportions.** Different samples of the same compound always contain its constituent elements in the same proportions by mass. (2.1)

**law of multiple proportions.** If two elements can combine to form more than one type of compound, the masses of one element that combine with a fixed mass of the other element are in ratios of small whole numbers. (2.1)

**Le Châtelier's principle.** If an external stress is applied to a system at equilibrium, the system will adjust itself in such a way as to partially offset the stress. (15.4)

**Lewis acid.** A substance that can accept a pair of electrons. (16.11)

**Lewis base.** A substance that can donate a pair of electrons. (16.11)

**Lewis dot symbol.** The symbol of an element with one or more dots that represent the number of valence electrons in an atom of the element. (9.1)

**Lewis structure.** A representation of covalent bonding using Lewis symbols. Shared electron pairs are shown either as lines or as pairs of dots between two atoms, and lone pairs are shown as pairs of dots on individual atoms. (9.4)

**ligand.** A molecule or an ion that is bonded to the metal ion in a complex ion. (20.2)

**limiting reagent.** The reactant used up first in a reaction. (3.9)

**line spectrum.** Spectrum produced when radiation is absorbed or emitted by a substance only at some wavelengths. (7.3)

**liter.** The volume occupied by 1 cubic decimeter. (1.5)

**lone pairs.** Valence electrons that are not involved in covalent bond formation. (9.4)

## M

**macroscopic properties.** Properties that can be measured directly. (1.5)

**manometer.** A device used to measure the pressure of gases. (5.2)

**many-electron atoms.** Atoms that contain two or more electrons. (7.5)

**mass.** A measure of the quantity of matter contained in an object. (1.5)

**mass defect.** The difference between the mass of an atom and the sum of the masses of its protons, neutrons, and electrons. (21.2)

**mass number.** The total number of neutrons and protons present in the nucleus of an atom. (2.3)

**matter.** Anything that occupies space and possesses mass. (1.3)

**melting point.** The temperature at which solid and liquid phases coexist in equilibrium. (12.6)

**metalloid.** An element with properties intermediate between those of metals and nonmetals. (2.4)

**metals.** Elements that are good conductors of heat and electricity and have the tendency to form positive ions in ionic compounds. (2.4)

**metathesis reaction.** A reaction that involves the exchange of parts between two compounds. (4.2)

**microscopic properties.** Properties that must be measured indirectly with the aid of a microscope or other special instrument. (1.5)

**miscible.** Two liquids that are completely soluble in each other in all proportions are said to be miscible. (13.2)

**mixture.** A combination of two or more substances in which the substances retain their identities. (1.3)

**moderator.** A substance that can reduce the kinetic energy of neutrons. (21.5)

**molality.** The number of moles of solute dissolved in 1 kilogram of solvent. (13.3)

**molar concentration.** See molarity.

**molar heat of fusion ( $\Delta H_{\text{fus}}$ ).** The energy (in kilojoules) required to melt 1 mole of a solid. (12.6)

**molar heat of sublimation ( $\Delta H_{\text{sub}}$ ).** The energy (in kilojoules) required to sublime 1 mole of a solid. (12.6)

**molar heat of vaporization ( $\Delta H_{\text{vap}}$ ).** The energy (in kilojoules) required to vaporize 1 mole of a liquid. (12.6)

**molar mass ( $M$ ).** The mass (in grams or kilograms) of 1 mole of atoms, molecules, or other particles. (3.2)

**molar solubility.** The number of moles of solute in 1 liter of a saturated solution (mol/L). (17.5)

**molarity ( $M$ ).** The number of moles of solute in 1 liter of solution. (4.5)

**mole (mol).** The amount of substance that contains as many elementary entities (atoms, molecules, or other particles) as there are atoms in exactly 12 grams (or 0.012 kilograms) of the carbon-12 isotope. (3.2)

**mole fraction.** Ratio of the number of moles of one component of a mixture to the total number of moles of all components in the mixture. (5.5)

**mole method.** An approach for determining the amount of product formed in a reaction. (3.8)

**molecular equations.** Equations in which the formulas of the compounds are written as though all species existed as molecules or whole units. (4.2)

**molecular formula.** An expression showing the exact numbers of atoms of each element in a molecule. (2.6)

**molecular mass.** The sum of the atomic masses (in amu) present in a given molecule. (3.3)

**molecular orbital.** An orbital that results from the interaction of atomic orbitals of the bonding atoms. (10.6)

**molecularity of a reaction.** The number of molecules reacting in an elementary step. (14.5)

**molecule.** An aggregate of at least two atoms in a definite arrangement held together by special forces. (2.5)

**monatomic ion.** An ion that contains only one atom. (2.5)

**monomer.** Simple repeating units in a polymer. (22.2)

**monoprotic acid.** Each unit of the acid yields one hydrogen ion. (4.3)

**multiple bonds.** Bonds formed when two atoms share two or more pairs of electrons. (9.4)

## N

**Nernst equation.** The relation between the emf of a galvanic cell and the standard emf and the concentrations of the oxidizing and reducing agents. (19.5)

**net ionic equation.** An equation that includes only the ionic species that actually take part in the reaction. (4.2)

**neutralization reaction.** A reaction between an acid and a base. (4.3)

**neutron.** A subatomic particle that bears no net electric charge. Its mass is slightly greater than a proton's. (2.2)

**Newton (N).** The SI unit for force. (5.2)

**noble gas core.** The noble gas that most nearly precedes the element being considered; used in writing electron configurations. (7.9)

**noble gases.** Nonmetallic elements in Group 8A (He, Ne, Ar, Kr, Xe, and Rn). (2.4)

**node.** A point at which the amplitude of a wave is zero. (7.4)

**nonelectrolyte.** A substance that, when dissolved in water, gives a solution that is not electrically conducting. (4.1)

**nonmetals.** Elements that are usually poor conductors of heat and electricity. (2.4)

**nonpolar molecule.** A molecule that does not possess a dipole moment. (10.2)

**nonvolatile.** Does not have a measurable vapor pressure. (13.6)

**nuclear binding energy.** The energy required to break up a nucleus into protons and neutrons. (21.2)

**nuclear chain reaction.** A self-sustaining sequence of nuclear fission reactions. (21.5)

**nuclear fission.** The process in which a heavy nucleus (mass number > 200) divides to

form small nuclei of intermediate mass and one or more neutrons. (21.5)

**nuclear fusion.** The combining of small nuclei into larger ones. (21.6)

**nuclear reaction.** A reaction involving change in an atomic nucleus. (21.1)

**nuclear transmutation.** The change undergone by a nucleus as a result of bombardment by neutrons or other particles. (21.1)

**nucleic acid.** High molar mass polymers that play an essential role in protein synthesis. (22.4)

**nucleotide.** The repeating unit in each strand of a DNA molecule which consists of a base-deoxyribose-phosphate group. (22.4)

**nucleus.** The central core of an atom. (2.2)

## O

**octet rule.** An atom other than hydrogen tends to form bonds until it is surrounded by eight valence electrons. (9.4)

**open system.** A system that can exchange mass and energy (usually in the form of heat) with its surroundings. (6.2)

**organic chemistry.** The branch of chemistry that deals with carbon compounds. (11.1)

**osmosis.** The net movement of solvent molecules through a semipermeable membrane from a pure solvent or from a dilute solution to a more concentrated solution. (13.6)

**osmotic pressure ( $\pi$ ).** The pressure required to stop osmosis. (13.6)

**overvoltage.** The additional voltage required to cause electrolysis. (19.8)

**oxidation number.** The number of charges an atom would have in a molecule if electrons were transferred completely in the direction indicated by the difference in electronegativity. (4.4)

**oxidation reaction.** The half-reaction that represents the loss of electrons in a redox process. (4.4)

**oxidation state.** See oxidation number.

**oxidation-reduction reaction.** See redox reaction.

**oxidizing agent.** A substance that can accept electrons from another substance or increase the oxidation numbers of another substance. (4.4)

**oxoacid.** An acid containing hydrogen, oxygen, and another element (the central element). (2.7)

**oxoanion.** An anion derived from an oxoacid. (2.7)

## P

**paramagnetic.** Attracted to a magnet. A paramagnetic substance contains one or more unpaired electrons. (7.8)

**partial pressure.** The pressure of one component in a mixture of gases. (5.5)

**Pascal (Pa).** A pressure of one newton per square meter ( $1 \text{ N/m}^2$ ). (5.2)

**Pauli exclusion principle.** No two electrons in an atom can have the same four quantum numbers. (7.8)

**percent composition.** The percent by mass of each element in a compound. (3.5)

**percent ionization.** The ratio of ionized acid concentration at equilibrium to the initial concentration of acid. (16.5)

**percent by mass.** The ratio of the mass of a solute to the mass of the solution, multiplied by 100%. (13.3)

**percent yield.** The ratio of the actual yield of a reaction to the theoretical yield, multiplied by 100%. (3.10)

**period.** A horizontal row of the periodic table. (2.4)

**periodic table.** A tabular arrangement of the elements by similarities in properties and by increasing atomic number. (2.4)

**pH.** The negative logarithm of the hydrogen ion concentration in an aqueous solution. (16.3)

**phase.** A homogeneous part of a system that is in contact with other parts of the system but separated from them by a well-defined boundary. (12.6)

**phase change.** Transformation from one phase to another. (12.6)

**phase diagram.** A diagram showing the conditions at which a substance exists as a solid, liquid, and vapor. (12.7)

**photoelectric effect.** A phenomenon in which electrons are ejected from the surface of certain metals exposed to light of at least a certain minimum frequency. (7.2)

**photon.** A particle of light. (7.2)

**physical equilibrium.** An equilibrium in which only physical properties change. (15.1)

**physical property.** Any property of a substance that can be observed without transforming the substance into some other substance. (1.4)

**pi bond ( $\pi$  bond).** A covalent bond formed by sideways overlapping orbitals; its electron density is concentrated above and below the plane of the nuclei of the bonding atoms. (10.5)

**pi molecular orbital.** A molecular orbital in which the electron density is concentrated above and below the line joining the two nuclei of the bonding atoms. (10.6)

**plasma.** A gaseous state of matter consisting of positive ions and electrons. (21.6)

**polar covalent bond.** In such a bond, the electrons spend more time in the vicinity of one atom than the other. (9.5)

**polar molecule.** A molecule that possesses a dipole moment. (10.2)

**polarimeter.** The instrument for studying interaction between plane-polarized light and chiral molecules. (11.5)

**polarizability.** The ease with which the electron distribution in the atom (or molecule) can be distorted. (12.2)

**polyatomic ion.** An ion that contains more than one atom. (2.5)

**polyatomic molecule.** A molecule that consists of more than two atoms. (2.5)

**polymer.** A molecular compound distinguished by a high molar mass and made up of many repeating units. (22.1)

**positron.** A particle that has the same mass as the electron but bears a +1 charge. (21.1)

**potential energy.** Energy available by virtue of an object's position. (6.1)

**precipitate.** An insoluble solid that separates from a supersaturated solution. (4.2)

**precipitation reaction.** A reaction characterized by the formation of a precipitate. (4.2)

**precision.** The closeness of agreement of two or more measurements of the same quantity. (1.6)

**pressure.** Force applied per unit area. (5.2)

**product.** The substance formed as a result of a chemical reaction. (3.7)

**protein.** A polymer of amino acids. (22.3)

**proton.** A subatomic particle having a single positive electric charge. The mass of a proton is about 1840 times that of an electron. (2.2)

## Q

**qualitative.** Consisting of general observations about the system. (1.2)

**qualitative analysis.** The determination of the types of ions present in a solution. (17.8)

**quantitative.** Comprising numbers obtained by various measurements of the system. (1.2)

**quantum.** The smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation. (7.1)

**quantum numbers.** Numbers that describe the distribution of electrons in atoms. (7.6)

## R

**racemic mixture.** An equimolar mixture of two enantiomers. (11.5)

**radiant energy.** Energy transmitted in the form of waves. (6.1)

**radiation.** The emission and transmission of energy through space in the form of particles and/or waves. (2.2)

**radical.** A species that contains an unpaired electron. (11.2)

**radioactive decay series.** A sequence of nuclear reactions that ultimately result in the formation of a stable isotope. (21.3)

**radioactivity.** The spontaneous breakdown of a nucleus by the emission of particles and/or radiation. (2.2)

**Raoult's law.** The partial pressure of the solvent over a solution is given by the

product of the vapor pressure of the pure solvent and the mole fraction of the solvent in the solution. (13.6)

**rare earth series.** See lanthanide series.

**rare gases.** See noble gases.

**rate constant.** Proportionality constant relating reaction rate to the concentrations of reactants. (14.2)

**rate law.** An expression relating the rate of a reaction to the rate constant and the concentrations of the reactants. (14.2)

**rate-determining step.** The slowest step in the sequence of steps leading to the formation of products. (14.5)

**reactants.** The starting substances in a chemical reaction. (3.7)

**reaction mechanism.** The sequence of elementary steps that leads to product formation. (14.5)

**reaction order.** The sum of the powers to which all reactant concentrations appearing in the rate law are raised. (14.2)

**reaction quotient ( $Q_c$ ).** A number equal to the ratio of product concentrations to reactant concentrations, each raised to the power of its stoichiometric coefficient at some point other than equilibrium. (15.3)

**reaction rate.** The change in concentration of reactant or product with time. (14.1)

**redox reaction.** A reaction in which there is either a transfer of electrons or a change in the oxidation numbers of the substances taking part in the reaction. Also called oxidation-reduction reaction. (4.4)

**reducing agent.** A substance that can donate electrons to another substance or decrease the oxidation numbers in another substance. (4.4)

**reduction reaction.** The half-reaction that represents the gain of electrons in a redox process. (4.4)

**representative elements.** Elements in Groups 1A through 7A, all of which have at least an incompletely filled *s* or *p* subshell of the highest principal quantum number. (8.2)

**resonance.** The use of two or more Lewis structures to represent a particular molecule. (9.8)

**resonance structure.** One of two or more alternative Lewis structures for a single molecule that cannot be described fully with a single Lewis structure. (9.8)

**reversible reaction.** A reaction that can occur in both directions. (4.1)

**ribonucleic acid (RNA).** A type of nucleic acid. (22.4)

**root-mean-square (rms) speed ( $u_{\text{rms}}$ ).** A measure of the average molecular speed at a given temperature. (5.6)

## S

**salt.** An ionic compound made up of a cation other than  $\text{H}^+$  and an anion other than  $\text{OH}^-$  or  $\text{O}^{2-}$ . (4.3)

**salt hydrolysis.** The reaction of the anion or cation, or both, of a salt with water. (16.9)

**saponification.** Soapmaking. (11.4)

**saturated hydrocarbons.** Hydrocarbons that contain only single covalent bonds. (11.2)

**saturated solution.** At a given temperature, the solution that results when the maximum amount of a substance has dissolved in a solvent. (13.1)

**scientific method.** A systematic approach to research. (1.2)

**second law of thermodynamics.** The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process. (18.4)

**second-order reaction.** A reaction whose rate depends on the concentration of one reactant raised to the second power or on the concentrations of two different reactants, each raised to the first power. (14.3)

**semipermeable membrane.** A membrane that allows solvent molecules to pass through, but blocks the movement of solute molecules. (13.6)

**sigma bond ( $\sigma$  bond).** A covalent bond formed by orbitals overlapping end-to-end; its electron density is concentrated between the nuclei of the bonding atoms. (10.5)

**sigma molecular orbital.** A molecular orbital in which the electron density is concentrated around a line between the two nuclei of the bonding atoms. (10.6)

**significant figures.** The number of meaningful digits in a measured or calculated quantity. (1.6)

**single bond.** Two atoms held together by one electron pair are joined by a single bond. (9.4)

**solubility.** The maximum amount of solute that can be dissolved in a given quantity of solvent at a specific temperature. (4.2, 17.5)

**solubility product ( $K_{\text{sp}}$ ).** The product of the molar concentrations of constituent ions, each raised to the power of its stoichiometric coefficient in the equilibrium equation. (17.5)

**solute.** The substance present in the smaller amount in a solution. (4.1)

**solution.** A homogeneous mixture of two or more substances. (4.1)

**solvation.** The process in which an ion or molecule is surrounded by solvent molecules arranged in an ordered manner. (13.2)

**solvent.** The substance present in the larger amount in a solution. (4.1)

**specific heat (*s*).** The amount of heat energy required to raise the temperature of one gram of a substance by one degree Celsius. (6.5)

**spectator ions.** Ions that are not involved in the overall reaction. (4.2)

**spectrochemical series.** A list of ligands arranged in order of their abilities to split the *d*-orbital energies. (20.4)

**standard atmospheric pressure (1 atm).**

The pressure that supports a column of mercury exactly 76 cm high at  $0^\circ\text{C}$  at sea level. (5.2)

**standard emf ( $E^\circ$ ).** The difference of the standard reduction potentials of the substance that undergoes reduction and the substance that undergoes oxidation in a redox process. (19.3)

**standard enthalpy of formation ( $\Delta H_f^\circ$ ).** The heat change that results when 1 mole of a compound is formed from its elements in their standard states. (6.6)

**standard enthalpy of reaction ( $\Delta H_{\text{rxn}}^\circ$ ).** The enthalpy change that occurs when a reaction is carried out under standard-state conditions. (6.6)

**standard entropy of reaction ( $\Delta S_{\text{rxn}}^\circ$ ).** The entropy change when the reaction is carried out under standard-state conditions. (18.4)

**standard free energy of formation ( $\Delta G_f^\circ$ ).**

The free-energy change when 1 mole of a compound is synthesized from its elements in their standard states. (18.5)

**standard free energy of reaction ( $\Delta G_{\text{rxn}}^\circ$ ).** The free energy change when the reaction is carried out under standard-state conditions. (18.5)

**standard reduction potential.** The voltage measured as a reduction reaction occurs at the electrode when all solutes are 1 *M* and all gases are at 1 atm. (19.3)

**standard solution.** A solution of accurately known concentration. (4.6)

**standard state.** The condition of 1 atm of pressure. (6.6)

**standard temperature and pressure (STP).**

$0^\circ\text{C}$  and 1 atm. (5.4)

**state function.** A property that is determined by the state of the system. (6.3)

**state of a system.** The values of all pertinent macroscopic variables (for example, composition, volume, pressure, and temperature) of a system. (6.3)

**stoichiometric amounts.** The exact molar amounts of reactants and products that appear in a balanced chemical equation. (3.9)

**stoichiometry.** The mass relationships among reactants and products in chemical reactions. (3.8)

**strong acid.** An acid that is a strong electrolyte. (16.4)

**strong base.** A base that is a strong electrolyte. (16.4)

**structural formula.** A representation that shows how atoms are bonded to one another in a molecule. (2.6)

**structural isomers.** Molecules that have the same molecular formula but different structures. (11.2)

**sublimation.** The process in which molecules go directly from the solid phase into the vapor phase. (12.6)

**substance.** A form of matter that has a definite or constant composition (the number and type of basic units present) and distinct properties. (1.3)

**supersaturated solution.** A solution that contains more of the solute than is present in a saturated solution. (13.1)

**surface tension.** The amount of energy required to stretch or increase the surface of a liquid by a unit area. (12.3)

**surroundings.** The rest of the universe outside a system. (6.2)

**system.** Any specific part of the universe that is of interest to us. (6.2)

## T

**termolecular reaction.** An elementary step involving three molecules. (14.5)

**ternary compounds.** Compounds consisting of three elements. (2.7)

**theoretical yield.** The amount of product predicted by the balanced equation when all of the limiting reagent has reacted. (3.10)

**theory.** A unifying principle that explains a body of facts and/or those laws that are based on them. (1.2)

**thermal energy.** Energy associated with the random motion of atoms and molecules. (6.1)

**thermal pollution.** The heating of the environment to temperatures that are harmful to its living inhabitants. (13.4)

**thermochemical equation.** An equation that shows both the mass and enthalpy relations. (6.4)

**thermochimistry.** The study of heat changes in chemical reactions. (6.2)

**thermodynamics.** The scientific study of the interconversion of heat and other forms of energy. (6.3)

**thermonuclear reactions.** Nuclear fusion reactions that occur at very high temperatures. (21.6)

**third law of thermodynamics.** The entropy of a perfect crystalline substance is

zero at the absolute zero of temperature. (18.4)

**titration.** The gradual addition of a solution of accurately known concentration to another solution of unknown concentration until the chemical reaction between the two solutions is complete. (4.6)

**tracers.** Isotopes, especially radioactive isotopes, that are used to trace the path of the atoms of an element in a chemical or biological process. (21.7)

**transition metals.** Elements that have incompletely filled *d* subshells or readily give rise to cations that have incompletely filled *d* subshells. (7.9)

**transition state.** See activated complex.

**transuranium elements.** Elements with atomic numbers greater than 92. (21.4)

**triple bond.** A covalent bond in which two atoms share three pairs of electrons. (9.4)

**triple point.** The point at which the vapor, liquid, and solid states of a substance are in equilibrium. (12.7)

**triprotic acid.** Each unit of the acid yields three hydrogen ions. (4.3)

## U

**unimolecular reaction.** An elementary step involving one molecule. (14.5)

**unit cell.** The basic repeating unit of the arrangement of atoms, molecules, or ions in a crystalline solid. (12.4)

**unsaturated hydrocarbons.** Hydrocarbons that contain carbon-carbon double bonds or carbon-carbon triple bonds. (11.2)

**unsaturated solution.** A solution that contains less solute than it has the capacity to dissolve. (13.1)

## V

**valence electrons.** The outer electrons of an atom, which are the ones involved in chemical bonding. (8.2)

**valence shell.** The outermost electron-occupied shell of an atom, which holds the electrons that are usually involved in bonding. (10.1)

**valence-shell electron-pair repulsion (VSEPR) model.** A model that accounts for the geometrical arrangements of shared and unshared electron pairs around a central atom in terms of the repulsive forces between electron pairs. (10.1)

**van der Waals equation.** An equation that describes the relationships among *P*, *V*, *n*, and *T* for a nonideal gas. (5.7)

**van der Waals forces.** The collective name for certain attractive forces between atoms and molecules, namely, dipole-dipole, dipole-induced dipole, and dispersion forces. (12.2)

**vaporization.** The escape of molecules from the surface of a liquid; also called evaporation. (12.6)

**viscosity.** A measure of a fluid's resistance to flow. (12.3)

**volatile.** Having a measurable vapor pressure. (13.6)

**volume.** Length cubed. (1.5)

## W

**wave.** A vibrating disturbance by which energy is transmitted. (7.1)

**wavelength ( $\lambda$ ).** The distance between identical points on successive waves. (7.1)

**weak acid.** An acid that is a weak electrolyte. (16.4)

**weak base.** A base that is a weak electrolyte. (16.4)

**weight.** The force that gravity exerts on an object. (1.5)

**work.** Directed energy change resulting from a process. (6.1)

# ANSWERS to Even-Numbered Problems

## Chapter 1

- 1.8** (a) Physical change. (b) Chemical change. (c) Physical change. (d) Chemical change. (e) Physical change. **1.10** (a) Extensive. (b) Intensive. (c) Intensive. **1.12** (a) Compound. (b) Element. (c) Compound. (d) Element. **1.18**  $1.30 \times 10^3$  g. **1.20** (a) (i) 386 K. (ii)  $3.10 \times 10^2$  K. (iii)  $6.30 \times 10^2$  K. (b) (i)  $-196^\circ\text{C}$ . (ii)  $-269^\circ\text{C}$ . (iii)  $328^\circ\text{C}$ . **1.22** (a)  $7.49 \times 10^{-1}$ . (b)  $8.026 \times 10^2$ . (c)  $6.21 \times 10^{-7}$ . **1.24** (a) 0.00003256. (b) 6,030,000. **1.26** (a)  $1.8 \times 10^{-2}$ . (b)  $1.14 \times 10^{10}$ . (c)  $-5 \times 10^4$ . (d)  $1.3 \times 10^3$ . **1.28** (a) Three. (b) One. (c) One or two. (d) Two. **1.30** (a) 1.28. (b)  $3.18 \times 10^{-3}$  mg. (c)  $8.14 \times 10^7$  dm. (d) 0.76 m/s. **1.32** (a)  $1.10 \times 10^8$  mg. (b)  $6.83 \times 10^{-5}$  m<sup>3</sup>. **1.34**  $3.1557 \times 10^7$  s. **1.36** (a) 81 in/s. (b)  $1.2 \times 10^2$  m/min. (c) 7.4 km/h. **1.38** (a)  $8.35 \times 10^{12}$  mi. (b)  $2.96 \times 10^3$  cm. (c)  $9.8 \times 10^8$  ft/s. (d)  $8.6^\circ\text{C}$ . (e)  $-459.67^\circ\text{F}$ . (f)  $7.12 \times 10^{-5}$  m<sup>3</sup>. (g)  $7.2 \times 10^3$  L. **1.40**  $6.25 \times 10^{-4}$  g/cm<sup>3</sup>. **1.42**  $4.35 \times 10^7$  ton. **1.44** 2.6 g/cm<sup>3</sup>. **1.46** 0.882 cm. **1.48** 10.5 g/cm<sup>3</sup>. **1.50** 767 mph. **1.52**  $75.6^\circ\text{F} \pm 0.2^\circ\text{F}$ . **1.54** 500 mL. **1.56**  $5.5 \times 10^{10}$  L. **1.58**  $-40^\circ$ . **1.60** (a) 0.5%. (b) 3.1%. **1.62**  $6.0 \times 10^{12}$  g Au;  $\$7.4 \times 10^{13}$ . **1.64** 30 times. **1.66**  $1.450 \times 10^{-2}$  mm. **1.68**  $2.3 \times 10^4$  kg NaF; 99%. **1.70**  $4.2 \times 10^{-19}$  g/L. **1.72** (a) First, data was collected. Then a hypothesis was formulated. (b) (i) Is there a similarly high Ir content at different locations on Earth? (ii) Are there simultaneous extinctions of other large species in addition to dinosaurs? (c) Yes, because the hypothesis has survived many experimental tests. (d)  $5.0 \times 10^{14}$  kg,  $5.5 \times 10^{11}$  tons;  $4 \times 10^3$  m. **1.74** 1725 sets;  $4.576 \times 10^4$  g. **1.76**  $4.97 \times 10^4$  g; alloy must be homogeneous in composition. **1.78** 0.13 L.

## Chapter 2

- 2.8** 0.62 mi. **2.12** 145. **2.14**  $^{15}\text{N}$ : 7 protons, 7 electrons, and 8 neutrons;  $^{33}\text{S}$ : 16 protons, 16 electrons, and 17 neutrons;  $^{63}\text{Cu}$ : 29 protons, 29 electrons, and 34 neutrons;  $^{84}\text{Sr}$ : 38 protons, 38 electrons, and 46 neutrons;  $^{130}\text{Ba}$ : 56 protons, 56 electrons, and 74 neutrons;  $^{186}\text{W}$ : 74 protons, 74 electrons, and 112 neutrons;  $^{202}\text{Hg}$ : 80 protons, 80 electrons, and 122 neutrons. **2.16** (a)  $^{186}\text{W}$ . (b)  $^{201}\text{Hg}$ . **2.22** (a) The metallic properties increase. (b) The metallic properties decrease. **2.24** Na, K; N, P; F, Cl. **2.30** (a) Diatomic molecule and compound. (b) Polyatomic molecule and compound. (c) Polyatomic molecule and element. **2.32** (a) H<sub>2</sub> and F<sub>2</sub>. (b) HCl and CO. (c) P<sub>4</sub> and S<sub>8</sub>. (d) H<sub>2</sub>O and C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>. **2.34** (protons, electrons): K<sup>+</sup> (19, 18); Mg<sup>2+</sup> (12, 10); Fe<sup>3+</sup> (26, 23); Br<sup>-</sup> (35, 36); Mn<sup>2+</sup> (25, 23); C<sup>4-</sup> (6, 10); Cu<sup>2+</sup> (29, 27). **2.42** (a) AlBr<sub>3</sub>. (b) NaSO<sub>2</sub>. (c) N<sub>2</sub>O<sub>5</sub>. (d) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. **2.44** C<sub>2</sub>H<sub>6</sub>O. **2.46** Ionic: NaBr, BaF<sub>2</sub>, CsCl. Molecular: CH<sub>4</sub>, CCl<sub>4</sub>, ICl, NF<sub>3</sub>. **2.48** (a) Potassium hypochlorite. (b) Silver carbonate. (c) Iron(II) chloride. (d) Potassium permanganate. (e) Cesium chlorate. (f) Hypoiodous acid. (g) Iron(II) oxide. (h) Iron(III) oxide. (i) Titanium(IV) chloride. (j) Sodium hydride. (k) Lithium nitride. (l) Sodium oxide. (m) Sodium peroxide. (n) Iron(III) chloride hexahydrate. **2.50** CuCN. (b) Sr(ClO<sub>2</sub>)<sub>2</sub>. (c) HClO<sub>4</sub>. (d) HI. (e) Na<sub>2</sub>NH<sub>4</sub>PO<sub>4</sub>. (f) PbCO<sub>3</sub>. (g) SnF<sub>2</sub>. (h) P<sub>4</sub>S<sub>10</sub>. (i) HgO. (j) Hg<sub>2</sub>I<sub>2</sub>. (k) CoCl<sub>2</sub> · 6H<sub>2</sub>O. **2.52** (c). **2.54** (a) H or H<sub>2</sub>? (b) NaCl is an ionic compound. **2.56** (a) Molecule and compound. (b) Element and molecule. (c) Element. (d) Molecule and compound. (e) Element. (f) Element

and molecule. (g) Element and molecule. (h) Molecule and compound. (i) Compound. (j) Element. (k) Element and molecule. (l) Compound. **2.58** (a) CO<sub>2</sub> (solid). (b) NaCl. (c) N<sub>2</sub>O. (d) CaCO<sub>3</sub>. (e) CaO. (f) Ca(OH)<sub>2</sub>. (g) NaHCO<sub>3</sub>. (h) Mg(OH)<sub>2</sub>. **2.60** (a) Metals in Groups 1A, 2A, and aluminum and nonmetals such as nitrogen, oxygen, and the halogens. (b) The transition metals. **2.62**  $^{23}\text{Na}$ . **2.64** Mercury (Hg) and bromine (Br<sub>2</sub>). **2.66** H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, O<sub>3</sub>, F<sub>2</sub>, Cl<sub>2</sub>, He, Ne, Ar, Kr, Xe, Rn. **2.68** He, Ne, and Ar are chemically inert and do not react with other elements. **2.70** All isotopes of radium are radioactive. It is a radioactive decay product of  $^{238}\text{U}$ . **2.72** (a) NaH (sodium hydride). (b) B<sub>2</sub>O<sub>3</sub> (diboron trioxide). (c) Na<sub>2</sub>S (sodium sulfide). (d) AlF<sub>3</sub> (aluminum fluoride). (e) OF<sub>2</sub> (oxygen difluoride). (f) SrCl<sub>2</sub> (strontium chloride). **2.74** (a) Bromine. (b) Radon. (c) Selenium. (d) Rubidium. (e) Lead. **2.76** 1.91  $\times 10^{-8}$  g. The change in mass is too small to measure accurately. **2.78** (a) Yes. (b) Ethane: CH<sub>3</sub>, C<sub>2</sub>H<sub>6</sub>. Acetylene: CH, C<sub>2</sub>H<sub>2</sub>. **2.80** Manganese (Mn).

## Chapter 3

- 3.6** 92.5%. **3.8**  $5.1 \times 10^{24}$  amu. **3.12**  $5.8 \times 10^3$  light-yr. **3.14**  $9.96 \times 10^{-15}$  mol Co. **3.16**  $3.01 \times 10^3$  g Au. **3.18** (a)  $1.244 \times 10^{-22}$  g/As atom. (b)  $9.746 \times 10^{-23}$  g/Ni atom. **3.20**  $2.98 \times 10^{22}$  Cu atoms. **3.22** Pb. **3.24** (a) 73.89 g. (b) 76.15 g. (c) 119.37 g. (d) 176.12 g. (e) 101.11 g. (f) 100.95 g. **3.26**  $6.69 \times 10^{21}$  C<sub>2</sub>H<sub>6</sub> molecules. **3.28** N:  $3.37 \times 10^{26}$  atoms; C:  $1.69 \times 10^{26}$  atoms; O:  $1.69 \times 10^{26}$  atoms; H:  $6.74 \times 10^{26}$  atoms. **3.30**  $8.56 \times 10^{22}$  molecules. **3.34** 7. **3.40** C: 10.06%; H: 0.8442%; Cl: 89.07%. **3.42** NH<sub>3</sub>. **3.44** C<sub>2</sub>H<sub>3</sub>NO<sub>5</sub>. **3.46** 39.3 g S. **3.48** 5.97 g F. **3.50** (a) CH<sub>2</sub>O. (b) KCN. **3.52** C<sub>6</sub>H<sub>6</sub>. **3.54** C<sub>5</sub>H<sub>8</sub>O<sub>4</sub>NNa. **3.60** (a)  $2\text{N}_2\text{O}_5 \longrightarrow 2\text{N}_2\text{O}_4 + \text{O}_2$ . (b)  $2\text{KNO}_3 \longrightarrow 2\text{KNO}_2 + \text{O}_2$ . (c)  $\text{NH}_4\text{NO}_3 \longrightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$ . (d)  $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$ . (e)  $2\text{NaHCO}_3 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$ . (f)  $\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \longrightarrow 4\text{H}_3\text{PO}_4$ . (g)  $2\text{HCl} + \text{CaCO}_3 \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$ . (h)  $2\text{Al} + 3\text{H}_2\text{SO}_4 \longrightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2$ . (i)  $\text{CO}_2 + 2\text{KOH} \longrightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$ . (j)  $\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ . (k)  $\text{Be}_2\text{C} + 4\text{H}_2\text{O} \longrightarrow 2\text{Be}(\text{OH})_2 + \text{CH}_4$ . (l)  $3\text{Cu} + 8\text{HNO}_3 \longrightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$ . (m)  $\text{S} + 6\text{HNO}_3 \longrightarrow \text{H}_2\text{SO}_4 + 6\text{NO}_2 + 2\text{H}_2\text{O}$ . (n)  $2\text{NH}_3 + 3\text{CuO} \longrightarrow 3\text{Cu} + \text{N}_2 + 3\text{H}_2\text{O}$ . **3.64** (d). **3.66** 1.01 mol. **3.68** 20 mol. **3.70** (a)  $2\text{NaHCO}_3 \longrightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ . (b) 78.3 g. **3.72** 255.9 g; 0.324 L. **3.74** 0.294 mol. **3.76** (a)  $\text{NH}_4\text{NO}_3 \longrightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$ . (b) 20 g N<sub>2</sub>O. **3.78** 18.0 g. **3.82** 6 mol NH<sub>3</sub>; 1 mol H<sub>2</sub>. **3.84** 0.709 g NO<sub>2</sub>; O<sub>3</sub>;  $6.9 \times 10^{-3}$  mol NO. **3.86** HCl; 23.4 g. **3.90** (a) 7.05 g. (b) 92.9%. **3.92** 20.6 g; 28.6%. **3.94** (b). **3.96** Cl<sub>2</sub>O<sub>7</sub>. **3.98** 18. **3.100** 65.4 amu; Zn. **3.102** 89.6%. **3.104** CH<sub>2</sub>O; C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>. **3.106** (a) Mn<sub>3</sub>O<sub>4</sub>. (b)  $3\text{MnO}_2 \longrightarrow \text{Mn}_3\text{O}_4 + \text{O}_2$ . **3.108** Mg<sub>3</sub>N<sub>2</sub> (magnesium nitride). **3.110**  $3.1 \times 10^{23}$  molecules/mol. **3.112** 4%. **3.114** (a) The less abundant isotope was undergoing radioactive decay. (b) 16 amu: CH<sub>4</sub>; 17 amu: NH<sub>3</sub>; 18 amu: H<sub>2</sub>O; 64 amu: SO<sub>2</sub>. (c) C<sub>3</sub>H<sub>8</sub>. A fragment (CH<sub>3</sub>) can break off from C<sub>3</sub>H<sub>8</sub>, but not from CO<sub>2</sub>. (d)  $\pm 0.030$  amu. (e) Do a mass spectrometry analysis of gold samples and compare the types and amounts of impurity elements present from different sources. **3.116** 9.6 g Fe<sub>2</sub>O<sub>3</sub>; 7.4 g KClO<sub>3</sub>.

## Chapter 4

- 4.8** (c). **4.10** (a) Strong electrolyte. (b) Nonelectrolyte. (c) Weak electrolyte. (d) Strong electrolyte. **4.12** (b) and (c). Ions have no mobility in the solid. **4.14** HCl does not ionize in benzene.
- 4.18** (b). **4.20** (a) Insoluble. (b) Soluble. (c) Soluble. (d) Insoluble. (e) Soluble. **4.22** (a) Ionic:  $2\text{Na}^+(\text{aq}) + \text{S}^{2-}(\text{aq}) + \text{Zn}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \longrightarrow \text{ZnS}(\text{s}) + 2\text{Na}^+(\text{aq}) + 2\text{Cl}^-(\text{aq})$ . Net ionic:  $\text{Zn}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq}) \longrightarrow \text{ZnS}(\text{s})$ . (b) Ionic:  $6\text{K}^+(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq}) + 3\text{Sr}^{2+}(\text{aq}) + 6\text{NO}_3^-(\text{aq}) \longrightarrow \text{Sr}_3(\text{PO}_4)_2(\text{s}) + 6\text{K}^+(\text{aq}) + 6\text{NO}_3^-(\text{aq})$ . Net ionic:  $3\text{Sr}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq}) \longrightarrow \text{Sr}_3(\text{PO}_4)_2(\text{s})$ . (c) Ionic:  $\text{Mg}^{2+}(\text{aq}) + 2\text{NO}_3^-(\text{aq}) + 2\text{Na}^+(\text{aq}) + 2\text{OH}^-(\text{aq}) \longrightarrow \text{Mg}(\text{OH})_2(\text{s}) + 2\text{Na}^+(\text{aq}) + 2\text{NO}_3^-(\text{aq})$ . Net ionic:  $\text{Mg}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \longrightarrow \text{Mg}(\text{OH})_2(\text{s})$ . **4.24** (a) Add chloride ions. (b) Add hydroxide ions. (c) Add carbonate ions. (d) Add sulfate ions. **4.32** (a) Brønsted base. (b) Brønsted base. (c) Brønsted acid. (d) Brønsted base and Brønsted acid.
- 4.34** (a)  $\text{CH}_3\text{COOH} + \text{K}^+ + \text{OH}^- \longrightarrow \text{K}^+ + \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$ ;  $\text{CH}_3\text{COOH} + \text{OH}^- \longrightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$ . (b)  $\text{H}_2\text{CO}_3 + 2\text{Na}^+ + 2\text{OH}^- \longrightarrow 2\text{Na}^+ + \text{CO}_3^{2-} + 2\text{H}_2\text{O}$ ;  $\text{H}_2\text{CO}_3 + 2\text{OH}^- \longrightarrow \text{CO}_3^{2-} + 2\text{H}_2\text{O}$ . (c)  $2\text{H}^+ + 2\text{NO}_3^- + \text{Ba}^{2+} + 2\text{OH}^- \longrightarrow \text{Ba}^{2+} + 2\text{NO}_3^- + 2\text{H}_2\text{O}$ ;  $2\text{H}^+ + 2\text{OH}^- \longrightarrow 2\text{H}_2\text{O}$ . **4.40** (a) Fe  $\longrightarrow \text{Fe}^{3+} + 3\text{e}^-$ ;  $\text{O}_2 + 4\text{e}^- \longrightarrow 2\text{O}^{2-}$ . Oxidizing agent:  $\text{O}_2$ ; reducing agent: Fe. (b)  $2\text{Br}^- \longrightarrow \text{Br}_2 + 2\text{e}^-$ ;  $\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$ . Oxidizing agent:  $\text{Cl}_2$ ; reducing agent:  $\text{Br}^-$ . (c) Si  $\longrightarrow \text{Si}^{4+} + 4\text{e}^-$ ;  $\text{F}_2 + 2\text{e}^- \longrightarrow 2\text{F}^-$ . Oxidizing agent:  $\text{F}_2$ ; reducing agent: Si. (d)  $\text{H}_2 \longrightarrow 2\text{H}^+ + 2\text{e}^-$ ;  $\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$ . Oxidizing agent:  $\text{Cl}_2$ ; reducing agent:  $\text{H}_2$ . **4.42** (a) +5, (b) +1, (c) +3, (d) +5, (e) +5, (f) +5. **4.44** All are zero. **4.46** (a) -3, (b)  $-\frac{1}{2}$ , (c) -1, (d) +4, (e) +3, (f) -2, (g) +3, (h) +6. **4.48** (b) and (d).
- 4.50** (a) No reaction. (b) No reaction. (c)  $\text{Mg} + \text{CuSO}_4 \longrightarrow \text{MgSO}_4 + \text{Cu}$ . (d)  $\text{Cl}_2 + 2\text{KBr} \longrightarrow \text{Br}_2 + 2\text{KCl}$ . **4.54** Dissolve 15.0 g NaNO<sub>3</sub> in enough water to make up 250 mL. **4.56** 10.8 g. **4.58** (a) 1.37 M. (b) 0.426 M. (c) 0.716 M. **4.60** (a) 6.50 g. (b) 2.45 g. (c) 2.65 g. (d) 7.36 g. (e) 3.95 g. **4.64** 0.0433 M. **4.66** 126 mL. **4.68** 1.09 M. **4.72** 35.72%. **4.74**  $2.31 \times 10^{-4}$  M. **4.78** 0.217 M. **4.80** (a) 6.00 mL. (b) 8.00 mL. **4.82** The Ba<sup>2+</sup> ions combine with the SO<sub>4</sub><sup>2-</sup> ions to form BaSO<sub>4</sub> precipitate.
- 4.84** Physical test: Only the NaCl solution would conduct electricity. Chemical test: Add AgNO<sub>3</sub> solution. Only the NaCl solution would give AgCl precipitate. **4.86** Mg, Na, Ca, Ba, K, or Li. **4.88** Oxidation number of C is +2 in CO and +4 (maximum) in CO<sub>2</sub>. **4.90** 1.26 M. **4.92** 0.171 M. **4.94** 0.115 M. **4.96** 0.80 L. **4.98** 1.73 M. **4.100** NaHCO<sub>3</sub>. NaOH is caustic and expensive. **4.102** 44.11% NaCl; 55.89% KCl. **4.104** (a) The precipitate CaSO<sub>4</sub> formed over Ca prevents the Ca from reacting with the sulfuric acid. (b) Aluminum is protected by a tenacious oxide layer (Al<sub>2</sub>O<sub>3</sub>). (c) These metals react more readily with water. (d) The metal should be placed below Fe and above H. **4.106** (a)  $8.320 \times 10^{-7}$  M. (b)  $3.286 \times 10^{-5}$  g. **4.108** 4.99 grains. **4.110** (a)  $\text{NH}_4^+ + \text{OH}^- \longrightarrow \text{NH}_3 + \text{H}_2\text{O}$ . (b) 97.99%. **4.112** Because the volume of the solution changes (increases or decreases) when the solid dissolves. **4.114** FeCl<sub>2</sub> · 4H<sub>2</sub>O. **4.116** (a) Reactions (2) and (4). (b) Reaction (5). (c) Reaction (3). (d) Reaction (1).

## Chapter 5

- 5.14** 0.797 atm; 80.8 kPa. **5.18** (1) b. (2) a. (3) c. (4) a. **5.20** 53 atm. **5.22** (a) 0.69 L. (b) 61 atm. **5.24**  $1.3 \times 10^2$  K. **5.26** ClF<sub>3</sub>. **5.32** 6.2 atm. **5.34** 472°C. **5.36** 1.9 atm. **5.38** 0.82 L. **5.40** 33.6 mL. **5.42**  $6.1 \times 10^{-3}$  atm. **5.44** 35.1 g/mol. **5.46** N<sub>2</sub>:  $2.1 \times 10^{22}$  molecules; O<sub>2</sub>:  $5.7 \times 10^{21}$  molecules; Ar:  $3 \times 10^{20}$  atoms. **5.48** 2.98 g/L. **5.50** SF<sub>4</sub>. **5.52** 18 g. **5.54** P<sub>2</sub>F<sub>4</sub>. **5.58** (a) 0.89 atm.

(b) 1.4 L. **5.60** 349 mmHg. **5.62** 19.8 g. **5.64** N<sub>2</sub>: 217 mmHg; H<sub>2</sub>: 650 mmHg. **5.72** N<sub>2</sub>: 472 m/s; O<sub>2</sub>: 441 m/s; O<sub>3</sub>: 360 m/s.

**5.74** Average speed: 2.7 m/s; rms speed: 2.8 m/s. Squaring favors the larger values compared to just taking the average value.

**5.80** Not ideal. Ideal gas pressure is 164 atm. **5.82**  $1.7 \times 10^2$  L. CO<sub>2</sub>: 0.49 atm; N<sub>2</sub>: 0.25 atm; H<sub>2</sub>O: 0.41 atm; O<sub>2</sub>: 0.041 atm.

**5.84** (a)  $\text{NH}_4\text{NO}_2(\text{s}) \longrightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ . (b) 0.273 g. **5.86** No. An ideal gas would not condense. **5.88** Higher in the winter because of reduced photosynthesis. **5.90** (a) 0.86 L.

(b)  $\text{NH}_4\text{HCO}_3(\text{s}) \longrightarrow \text{NH}_3(\text{g}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ . Advantage: more gases (CO<sub>2</sub> and NH<sub>3</sub>) generated; disadvantage: odor of ammonia! **5.92** 3.88 L. **5.94** (a)  $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$ . (b) 11.4 L. **5.96** O<sub>2</sub>: 0.166 atm; NO<sub>2</sub>: 0.333 atm. **5.98** (a)  $\text{CO}_2(\text{g}) + \text{CaO}(\text{s}) \longrightarrow \text{CaCO}_3(\text{s})$ ;  $\text{CO}_2(\text{g}) + \text{BaO}(\text{s}) \longrightarrow \text{BaCO}_3(\text{s})$ . (b) 10.5% CaO; 89.5% BaO.

**5.100**  $1.7 \times 10^{12}$  O<sub>2</sub> molecules. **5.102** Ne, because it has the smallest  $a$  value. **5.104** 53.4%. **5.106** 1072 mmHg.

**5.108** 43.8 g/mol; CO<sub>2</sub>. **5.110** (a) No. Temperature is a statistical concept. (b) (i) Both are the same. (ii) The He atoms in V<sub>1</sub> collide with the walls more frequently. (c) (i) The rms speed is greater at T<sub>2</sub>. (ii) The He atoms at T<sub>2</sub> collide with the walls more frequently and with greater force. (d) (i) False. (ii) True. (iii) True.

**5.112** (a)  $u_{\text{mp}}$ : 421 m/s.  $u_{\text{rms}}$ : 515 m/s. (b) 1200 K.

**5.114** (a)  $8(4\pi r^3/3)$ . (b)  $4N_A(4\pi r^3/3)$ . The excluded volume is 4 times the volume of the atoms. **5.116** NO. **5.118** (b).

## Chapter 6

**6.16** (a) 0. (b) -9.5 J. (c) -18 J. **6.18** 48 J. **6.20**  $-3.1 \times 10^3$  J.

**6.26**  $1.57 \times 10^4$  kJ. **6.28** 0; -553.8 kJ/mol. **6.32** A. **6.34** 728 kJ.

**6.36** 50.7°C. **6.38** 26.3°C. **6.46** O<sub>2</sub>. **6.48** (a)  $\Delta H_f^\circ[\text{Br}_2(\text{l})] = 0$ ;  $\Delta H_f^\circ[\text{Br}_2(\text{g})] > 0$ . (b)  $\Delta H_f^\circ[\text{I}_2(\text{s})] = 0$ ;  $\Delta H_f^\circ[\text{I}_2(\text{g})] > 0$ .

**6.50** Measure  $\Delta H^\circ$  for the formation of Ag<sub>2</sub>O from Ag and O<sub>2</sub> and of CaCl<sub>2</sub> from Ca and Cl<sub>2</sub>. **6.52** (a) -167.2 kJ/mol.

(b) -56.2 kJ/mol. **6.54** (a) -1411 kJ/mol. (b) -1124 kJ/mol.

**6.56** 218.2 kJ/mol. **6.58** 4.51 kJ/g. **6.60**  $2.70 \times 10^2$  kJ.

**6.62** -84.6 kJ/mol. **6.64** -847.6 kJ/mol. **6.66**  $\Delta H_2 - \Delta H_1$ .

**6.68** (a) -336.5 kJ/mol. (b) NH<sub>3</sub>. **6.70** 43.6 kJ. **6.72** 0.

**6.74** -350.7 kJ/mol. **6.76** 0.492 J/g · °C. **6.78** The first (exothermic) reaction can be used to promote the second (endothermic) reaction.

**6.80**  $1.09 \times 10^4$  L. **6.82** 5.60 kJ/mol. **6.84** (a) **6.86** (a) A more fully packed freezer has a greater mass and hence a larger heat capacity. (b) Tea or coffee has a greater amount of water, which has a higher specific heat than noodles. **6.88** -1.84 × 10<sup>3</sup> kJ. **6.90**  $3.0 \times 10^9$ . **6.92** 5.35 kJ/°C. **6.94** -5.2 × 10<sup>6</sup> kJ.

**6.96** (a)  $1.4 \times 10^2$  kJ. (b)  $3.9 \times 10^2$  kJ. **6.98** 104 g. **6.100** 9.9 × 10<sup>8</sup> J; 304°C. **6.102** (a)  $\text{CaC}_2 + 2\text{H}_2\text{O} \longrightarrow \text{C}_2\text{H}_2 + \text{Ca}(\text{OH})_2$ .

(b)  $1.51 \times 10^3$  kJ. **6.104** (a)  $\Delta E = w$ . The system does work on the surroundings and decreases its internal energy. The water cools to form snow. (b) Just the opposite of (a). (c) First set  $q = (1/2)mu^2$ . Next, show stopping distance,  $d$ , to be proportional to  $q$  and hence to  $u^2$ . As  $u$  increases to 2 $u$ ,  $d$  increases to 4 $u^2$ , which is proportional to 4 $d$ . **6.106** The deserts, unlike coastal regions, have very low humidity and cannot retain heat because sand and rocks have smaller specific heat, than water. **6.108** 96.21%.

**6.110** (a) CH. (b) 49 kJ/mol. **6.112** -101.3 J. Yes, because in a cyclic process, the change in a state function must be zero.

## Chapter 7

**7.8** (a)  $6.58 \times 10^{14}$ /s. (b)  $1.22 \times 10^8$  nm. **7.10** 2.5 min. **7.12** 4.95 × 10<sup>14</sup>/s. **7.16** (a)  $4.0 \times 10^2$  nm. (b)  $5.0 \times 10^{-19}$  J. **7.18** 1.2 × 10<sup>2</sup> nm (UV). **7.20** (a)  $3.70 \times 10^2$  nm;  $3.70 \times 10^{-7}$  m. (b) UV.

(c)  $5.38 \times 10^{-19}$  J. **7.26** Use a prism. **7.28** Compare the emission

spectra with those on Earth of known elements. **7.30**  $3.027 \times 10^{-19}$  J. **7.32**  $6.17 \times 10^{14}$  s; 486 nm. **7.34** 5. **7.40**  $1.37 \times 10^{-6}$  nm. **7.42**  $1.7 \times 10^{-23}$  nm. **7.54**  $\ell = 2$ :  $m_\ell = -2, -1, 0, 1, 2$ .  $\ell = 1$ :  $m_\ell = -1, 0, 1$ .  $\ell = 0$ :  $m_\ell = 0$ . **7.56** (a)  $n = 3$ ,  $\ell = 0$ ,  $m_\ell = 0$ . (b)  $n = 4$ ,  $\ell = 1$ ,  $m_\ell = -1, 0, 1$ . (c)  $n = 3$ ,  $\ell = 2$ ,  $m_\ell = -2, -1, 0, 1, 2$ . In all cases,  $m_s = +\frac{1}{2}$  or  $-\frac{1}{2}$ . **7.58** Differ in orientation only. **7.60**  $6s$ ,  $6p$ ,  $6d$ ,  $6f$ ,  $6g$ , and  $6h$ . **7.62**  $2n^2$ . **7.64** (a) 3. (b) 6. (c) 0. **7.66** There is no shielding in an H atom. **7.68** (a)  $2s < 2p$ . (b)  $3p < 3d$ . (c)  $3s < 4s$ . (d)  $4d < 5f$ . **7.80** Al:  $1s^2 2s^2 2p^6 3s^2 3p^1$ . B:  $1s^2 2s^2 2p^1$ . F:  $1s^2 2s^2 2p^5$ . **7.82** B(1), Ne(0), P(3), Sc(1), Mn(5), Se(2), Kr(0), Fe(4), Cd(0), I(1), Pb(2). **7.84** Ge:  $[\text{Ar}]4s^2 3d^{10} 4p^2$ . Fe:  $[\text{Ar}]4s^2 3d^6$ . Zn:  $[\text{Ar}]4s^2 3d^{10}$ . Ni:  $[\text{Ar}]4s^2 3d^8$ . W:  $[\text{Xe}]6s^2 4f^4 5d^4$ . Ti:  $[\text{Xe}]6s^2 4f^4 5d^{10} 6p^1$ . **7.86** S<sup>+</sup>. **7.92**  $[\text{Kr}]5s^2 4d^5$ . **7.94** (a) An e in a 2s and an e in each 2p orbital. (b) 2 e each in a 4p, a 4d, and a 4f orbital. (c) 2 e in each of the 5 3d orbitals. (d) An e in a 2s orbital. (e) 2 e in a 4f orbital. **7.96** Wave properties. **7.98** (a)  $1.05 \times 10^{-25}$  nm. (b)  $8.86$  nm. **7.100** (a)  $1.20 \times 10^{18}$  photons. (b)  $3.76 \times 10^8$  W. **7.102** 419 nm. In principle, yes; in practice, no. **7.104**  $3.0 \times 10^{19}$  photons. **7.106** He<sup>+</sup>: 164 nm, 121 nm, 109 nm, 103 nm (all in the UV region). H: 657 nm, 487 nm, 434 nm, 411 nm (all in the visible region). **7.108**  $1.2 \times 10^2$  photons. **7.110** Yellow light will generate more electrons; blue light will generate electrons with greater kinetic energy. **7.112**  $7.39 \times 10^{-2}$  nm. **7.114** 0.929 pm;  $3.23 \times 10^{20}$ /s. **7.116** (b) and (d). **7.118** 10.6 nm. **7.120**  $3.87 \times 10^5$  m/s.

## Chapter 8

- 8.16** (a)  $1s^2 2s^2 2p^6 3s^2 3p^5$ . (b) Representative element. (c) Paramagnetic. **8.18** (a) and (d); (b) and (e); (c) and (f). **8.20** (a) Group 1A. (b) Group 5A. (c) Group 8A. (d) Group 8B. **8.22** Fe. **8.28** (a) [Ne]. (b) [Ne]. (c) [Ar]. (d) [Ar]. (e) [Ar]. (f)  $[\text{Ar}]3d^6$ . (g)  $[\text{Ar}]3d^9$ . (h)  $[\text{Ar}]3d^{10}$ . **8.30** (a) Cr<sup>3+</sup>. (b) Sc<sup>3+</sup>. (c) Rh<sup>3+</sup>. (d) Ir<sup>3+</sup>. **8.32** Be<sup>2+</sup> and He; F<sup>-</sup> and N<sup>3-</sup>; Fe<sup>2+</sup> and Co<sup>3+</sup>; S<sup>2-</sup> and Ar. **8.38** Na > Mg > Al > P > Cl. **8.40** F. **8.42** The effective nuclear charge on the outermost electrons increases from left to right as a result of incomplete shielding by the inner electrons. **8.44** Mg<sup>2+</sup> < Na<sup>+</sup> < F<sup>-</sup> < O<sup>2-</sup> < N<sup>3-</sup>. **8.46** Te<sup>2-</sup>. **8.48** -199.4°C. **8.52** The 3p<sup>1</sup> electron of Al is effectively shielded by the inner electrons and 3s<sup>2</sup> electrons. **8.54** 2080 kJ/mol is for  $1s^2 2s^2 2p^6$ . **8.56**  $8.43 \times 10^6$  kJ/mol. **8.60** Cl. **8.62** Alkali metals have  $n_s^1$  and so can accept another electron. **8.66** Low ionization energy, reacts with water to form FrOH, and with oxygen to form oxide and superoxide. **8.68** The  $ns^1$  electron of Group 1B metals is incompletely shielded by the inner d electrons and therefore they have much higher first ionization energies. **8.70** (a)  $\text{Li}_2\text{O}(s) + \text{H}_2\text{O}(l) \longrightarrow 2\text{LiOH}(aq)$ . (b)  $\text{CaO}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{Ca}(\text{OH})_2(aq)$ . (c)  $\text{CO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{CO}_3(aq)$ . **8.72** BaO. Ba is more metallic. **8.74** (a) Bromine. (b) Nitrogen. (c) Rubidium. (d) Magnesium. **8.76** (a) Mg<sup>2+</sup> < Na<sup>+</sup> < F<sup>-</sup> < O<sup>2-</sup>. (b) O<sup>2-</sup> < F<sup>-</sup> < Na<sup>+</sup> < Mg<sup>2+</sup>. **8.78** M is potassium (K) and X is bromine (Br<sub>2</sub>). **8.80** O<sup>+</sup> and N; Ar and S<sup>2-</sup>; Ne and N<sup>3-</sup>; Zn and As<sup>3+</sup>; Cs<sup>+</sup> and Xe. **8.82** (a) and (d). **8.84** First: bromine; second: iodine; third: chlorine; fourth: fluorine. **8.86** Fluorine. **8.88** H<sup>-</sup>. **8.90** Li<sub>2</sub>O (basic), BeO (amphoteric), B<sub>2</sub>O<sub>3</sub> (acidic), CO<sub>2</sub> (acidic), N<sub>2</sub>O<sub>5</sub> (acidic). **8.92** It can form H<sup>+</sup> and H<sup>-</sup> ions. **8.94** 418 kJ/mol. Vary the frequency. **8.96** About 23°C. **8.98** (a) Mg [in Mg(OH)<sub>2</sub>]. (b) Liquid Na, (c) Mg (in MgSO<sub>4</sub> · 7H<sub>2</sub>O). (d) Na (in NaHCO<sub>3</sub>). (e) K (in KNO<sub>3</sub>). (f) Mg. (g) Ca (in CaO). (h) Ca. (i) Na (in NaCl); Ca (in CaCl<sub>2</sub>). **8.100** Physical properties: solid, high m.p.; 2NaAt + 2H<sub>2</sub>SO<sub>4</sub> → At<sub>2</sub> + SO<sub>2</sub> + Na<sub>2</sub>SO<sub>4</sub> + 2H<sub>2</sub>O. **8.102** 242 nm. **8.104** (a) F<sub>2</sub>. (b) Na. (c) B. (d) N<sub>2</sub>. (e) Al. **8.106** (a) Use a discharge tube and compare the emission spectrum of Ar with other elements.

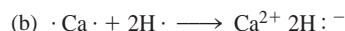
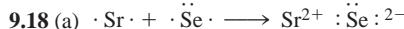
(b) Ar is inert. (c) With the discovery of Ar, Ramsay realized there may be other unreactive gases belonging to the same periodic group. (d) Being a light gas, helium's concentration in the atmosphere is very low. It is chemically inert. (e) Radon is unreactive toward most elements and its has a short half-life.

**8.108** 419 nm. **8.110** To prepare NH<sub>3</sub>, isolate N<sub>2</sub> from air and obtain H<sub>2</sub> by electrolyzing water. Combine N<sub>2</sub> and H<sub>2</sub> to form NH<sub>3</sub>. To prepare HNO<sub>3</sub>, first combine N<sub>2</sub> and O<sub>2</sub> to form NO, which is further oxidized to NO<sub>2</sub>. Next, react NO<sub>2</sub> with water to form HNO<sub>2</sub> and HNO<sub>3</sub>. Finally, combine NH<sub>3</sub> and HNO<sub>3</sub> to form NH<sub>4</sub>NO<sub>3</sub>.

## Chapter 9

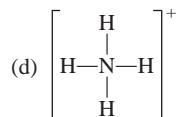
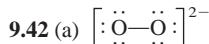
**9.16** (a) RbI, rubidium iodide. (b) Cs<sub>2</sub>SO<sub>4</sub>, cesium sulfate.

(c) Sr<sub>3</sub>N<sub>2</sub>, strontium nitride. (d) Al<sub>2</sub>S<sub>3</sub>, aluminum sulfide.

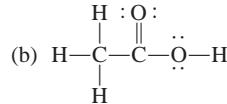


**9.20** (a) BF<sub>3</sub>, covalent. Boron trifluoride. (b) KBr, ionic. Potassium bromide. **9.26** 2195 kJ/mol. **9.34** C—H < Br—H < F—H <

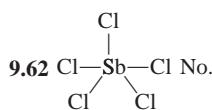
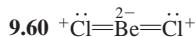
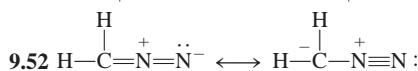
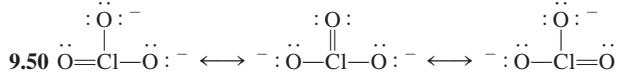
Li—Cl < Na—Cl < K—F. **9.36** Cl—Cl < Br—Cl < Si—C < Cs—F. **9.38** (a) Covalent. (b) Polar covalent. (c) Ionic. (d) Polar covalent.

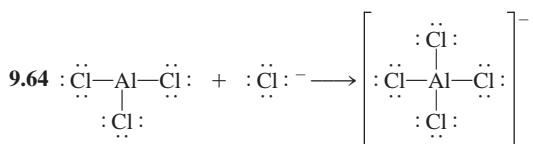


**9.44** (a) Neither O atom has a complete octet; one H atom forms a double bond.



**9.48** (1) The C atom has a lone pair. (2) The negative charge is on the less electronegative C atom.

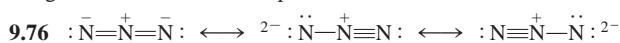




9.68 303.0 kJ/mol. 9.70 (a) -2759 kJ/mol. (b) -2855 kJ/mol.

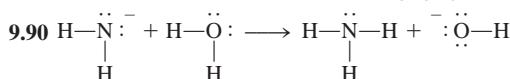
9.72 Covalent:  $\text{SiF}_4$ ,  $\text{PF}_5$ ,  $\text{SF}_6$ ,  $\text{ClF}_3$ ; ionic:  $\text{NaF}$ ,  $\text{MgF}_2$ ,  $\text{AlF}_3$ .

9.74 KF is a solid; has a high melting point; is an electrolyte.  $\text{CO}_2$  is a gas; it is a molecular compound.

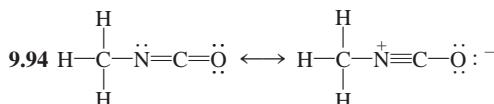


9.78 (a)  $\text{AlCl}_4^-$ . (b)  $\text{AlF}_6^{3-}$ . (c)  $\text{AlCl}_3$ . 9.80 C has incomplete octet in  $\text{CF}_2$ ; C has an expanded octet in  $\text{CH}_5$ ; F and H can only form a single bond; the I atoms are too large to surround the P atom. 9.82 (a) False. (b) True. (c) False. (d) False. 9.84 -67 kJ/mol.

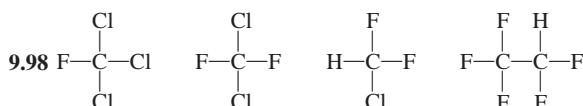
9.86  $\text{N}_2$ . 9.88  $\text{NH}_4^+$  and  $\text{CH}_4$ ; CO and  $\text{N}_2$ ;  $\text{B}_3\text{N}_3\text{H}_6$  and  $\text{C}_6\text{H}_6$ .



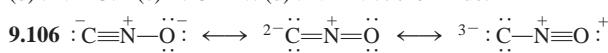
9.92 F cannot form an expanded octet.



9.96 (a) Important. (b) Important. (c) Not important. (d) Not important.

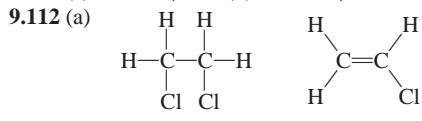


9.100 (a) -9.2 kJ/mol. (b) -9.2 kJ/mol. 9.102 (a)  $^-:\text{C}\equiv\text{O}:^+$  (b)  $:\text{N}\equiv\text{O}:^+$  (c)  $^-:\text{C}\equiv\text{N}:^-$  (d)  $:\text{N}\equiv\text{N}^-:\text{N}^+$  9.104 True.



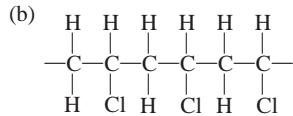
The importance decreases from left to right. 9.108 347 kJ/mol.

9.110 (a) -107 kJ/mol. (b) -92.6 kJ/mol.

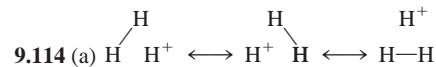


ethylene dichloride    vinyl chloride

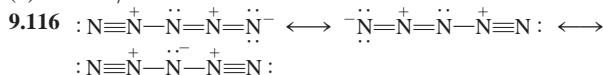
C—C bond covalent; C—H and C—Cl bonds polar.



(c)  $-1.2 \times 10^6$  kJ. This process generates a great deal of heat. The design would need to incorporate a means of cooling the reaction vessel.



(b) -413 kJ/mol.



## Chapter 10

10.8 (a) Trigonal planar. (b) Linear. (c) Tetrahedral.

10.10 (a) Tetrahedral. (b) Bent. (c) Trigonal planar. (d) Linear.

(e) Square planar. (f) Tetrahedral. (g) Trigonal bipyramidal.

(h) Trigonal pyramidal. (i) Tetrahedral. 10.12  $\text{SiCl}_4$ ,  $\text{Cl}_4$ ,  $\text{CdCl}_4^{2-}$ .

10.18 Electronegativity decreases from F to I. 10.20 Higher.

10.22 (b) = (d) < (c) < (a). 10.32  $sp^3$  for both Si atoms.

10.34 B:  $sp^2$  to  $sp^3$ ; N: remains  $sp^3$ . 10.36 (a)  $sp^3$ . (b)  $sp^3$ ,  $sp^2$ ,  $sp^2$ .

(c)  $sp^3$ ,  $sp$ ,  $sp$ ,  $sp^3$ . (d)  $sp^3$ ,  $sp^2$ . (e)  $sp^3$ ,  $sp^2$ . 10.38  $sp$ . 10.40  $sp^3d$ .

10.42 Nine pi bonds and nine sigma bonds. 10.48 Electron spins must be paired in  $\text{H}_2$ . 10.50  $\text{Li}_2^- = \text{Li}_2^+ < \text{Li}_2$ . 10.52  $\text{B}_2^+$ . 10.54 Only MO theory predicts  $\text{O}_2$  to be paramagnetic. 10.56  $\text{O}_2^{2-} < \text{O}_2^- < \text{O}_2 < \text{O}_2^+$ . 10.58  $\text{B}_2$  contains a pi bond;  $\text{C}_2$  contains two pi bonds.

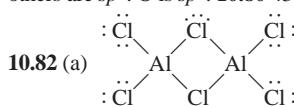
10.60 Linear. Dipole moment measurement. 10.62 The large size of Si results in poor sideways overlap of  $p$  orbitals to form pi bonds.

10.64  $\text{XeF}_3$ : T-shaped;  $\text{XeF}_5^+$ : square pyramidal;  $\text{SbF}_6^-$ : octahedral.

10.66 (a) 180°. (b) 120°. (c) 109.5°. (d) About 109.5°. (e) 180°.

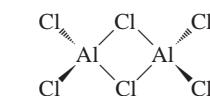
(f) About 120°. (g) About 109.5°. (h) 109.5°. 10.68  $sp^3d$ . 10.70  $\text{ICl}_2$  and  $\text{CdBr}_2$ . 10.72 (a)  $sp^2$ . (b) Molecule on the right. 10.74 The pi bond in cis-dichloroethylene prevents rotation. 10.76 Si has 3d orbitals so water can add to Si (valence shell expansion).

10.78 C:  $sp^2$ ; N: N atom that forms a double bond is  $sp^2$ , the others are  $sp^3$ . O is  $sp^2$ . 10.80 43.6%.



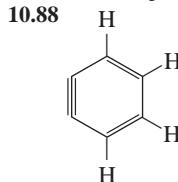
(b) The hybridization of Al in  $\text{AlCl}_3$  is  $sp^2$ . The molecule is trigonal planar. The hybridization of Al in  $\text{Al}_2\text{Cl}_6$  is  $sp^3$ .

(c) The geometry about each Al atom is tetrahedral.



(d) The molecules are nonpolar; they do not possess a dipole moment.

10.84 The double bonded C atoms (4) are  $sp^2$  hybridized. The rest are all  $sp^3$  hybridized. 10.86 (a) A  $\sigma$  bond is formed by end-to-end overlaps. Rotation will not break this overlap. A  $\pi$  bond is formed by sideways overlap. The two 90° rotations will break and then reform the  $\pi$  bond. (b) The  $\pi$  bond is weaker because of the lesser extent of overlap. (c) 444 nm.



The normal bond angle for a hexagon is 60°. However, the triple bond requires an angle of 180° (linear) and therefore there is a great deal of strain in the molecule. Consequently, the molecule is very reactive (breaking the bond to relieve the strain).

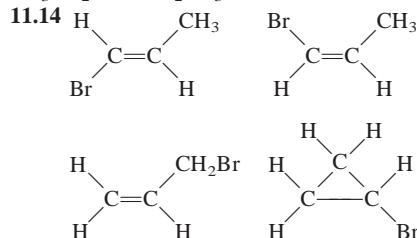
10.90 The Lewis structure shows four pairs of electrons on the two oxygen atoms. From Table 10.5 we see that these eight valence electrons are placed in the  $\sigma_{2p_x}$ ,  $\pi_{2p_y}$ ,  $\pi_{2p_z}$ ,  $\pi_{2p_y}^*$ , and  $\pi_{2p_z}^*$  orbitals. For all the electrons to be paired, energy is needed to flip the spin

in one of the antibonding molecular orbitals ( $\pi_{2p_x}^*$  or  $\pi_{2p_z}^*$ ). According to Hund's rule, this arrangement is less stable than the ground-state configuration. Hence, the Lewis structure shown actually corresponds to an excited state of the oxygen molecule.

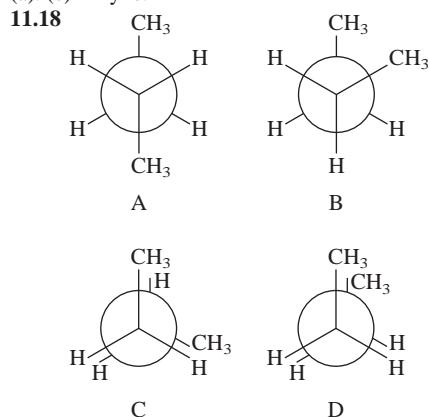
**10.92** (a) Although the O atoms are  $sp^3$ -hybridized, they are locked in a planar structure by the benzene rings. The molecule is symmetrical and therefore does not possess a dipole moment.  
 (b) 20  $\sigma$  bonds and 6  $\pi$  bonds.

## Chapter 11

**11.12**  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ ;  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHClCH}_3$ ;  $\text{CH}_3\text{CH}_2\text{CHClCH}_2\text{CH}_3$ .



**11.16** (a) Alkene or cycloalkane. (b) Alkyne. (c) Alkane. (d) Like (a). (e) Alkyne.



Stability decreases from A to D. **11.20** No. The bond angles are too small. **11.22** (a) is alkane and (b) is alkene. Only an alkene reacts with a hydrogen halide. **11.24**  $-630.8 \text{ kJ/mol}$ . **11.26** (a) *cis*-1,2-dichlorocyclopropane. (b) *trans*-1,2-dichlorocyclopropane.

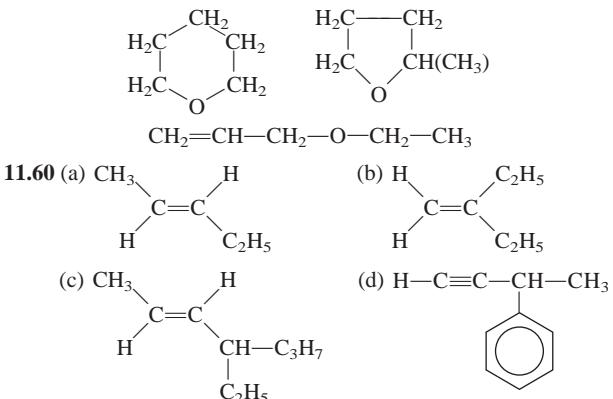
**11.28** (a) 2-methylpentane. (b) 2,3,4-trimethylhexane.  
 (c) 3-ethylhexane. (d) 3-bromo-1-pentene. (e) 2-pentyne.

**11.32** (a) 1,3-dichloro-4-methylbenzene. (b) 2-ethyl-1,4-dinitrobenzene. (c) 1,2,4,5-tetramethylbenzene. (d) 3-phenyl-1-butene. **11.36** (a) Ether. (b) Amine. (c) Aldehyde. (d) Ketone.  
 (e) Carboxylic acid. (f) Alcohol. (g) Amino acid (amine and carboxylic acid). **11.38**  $\text{HCOOH} + \text{CH}_3\text{OH} \longrightarrow \text{HCOOCH}_3 + \text{H}_2\text{O}$ . Methyl formate. **11.40**  $(\text{CH}_3)_2\text{CH}-\text{O}-\text{CH}_3$ .

**11.42** (a) Ketone. (b) Ester. (c) Ether. **11.46** (a) The C atoms bonded to the methyl group and the amino group and the H atom. (b) The C atoms bonded to Br. **11.48**  $-174 \text{ kJ/mol}$ .

**11.50**  $\text{--CF}_2-\text{CF}_2-$ . **11.52** (a) Rubbing alcohol. (b) Vinegar.  
 (c) Moth balls. (d) Organic synthesis. (e) Solvent. (f) Antifreeze.  
 (g) Natural gas. (h) Synthetic polymer. **11.54** (a) 3. (b) 16.  
 (c) 6. **11.56** (a) C: 15.81 mg; H: 1.33 mg; O: 3.49 mg. (b)  $\text{C}_6\text{H}_6\text{O}$ .  
 (c) Phenol. **11.58** Empirical and molecular formula:

$\text{C}_5\text{H}_{10}\text{O}$ .

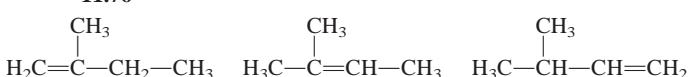


**11.62**  $\text{CH}_3\text{CH}_2\text{CHO}$ . **11.64** (a) Alcohol. (b) Ether. (c) Aldehyde.

(d) Carboxylic acid. (e) Amine. **11.66** The acids in lemon juice convert the amines to the ammonium salts, which have very low vapor pressures. **11.68** Methane ( $\text{CH}_4$ ); ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ); methanol ( $\text{CH}_3\text{OH}$ ); isopropanol ( $\text{C}_3\text{H}_7\text{OH}$ ); ethylene glycol ( $\text{CH}_2\text{OHCH}_2\text{OH}$ ); naphthalene ( $\text{C}_{10}\text{H}_8$ ); acetic acid ( $\text{CH}_3\text{COOH}$ ).

**11.70** (a) One. (b) Two. (c) Five. **11.72**  $\text{Br}_2$  dissociates into Br atoms, which react with  $\text{CH}_4$  to form  $\text{CH}_3\text{Br}$  and  $\text{HBr}$ . **11.74** (a) Reaction between glycerol and carboxylic acid to form an ester. (b) Fat or oil (see problem for structure) +  $\text{NaOH}(aq) \longrightarrow$  glycerol + 3  $\text{RCOO}^- \text{Na}^+$  (soap). (c) Molecules having more  $\text{C}=\text{C}$  bonds are harder to pack tightly. Consequently, they have a lower melting point. (d) Use  $\text{H}_2$  and a catalyst. (e) 123.

**11.76**



**11.78**  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  or  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ .

## Chapter 12

**12.8** Methane; it has the lowest boiling point. **12.10** (a) Dispersion forces. (b) Dispersion and dipole-dipole forces. (c) Same as (b). (d) Ionic and dispersion forces. (e) Dispersion forces. **12.12** (e).

**12.14** Only 1-butanol can form hydrogen bonds so it has a higher boiling point. **12.16** (a) Xe (greater dispersion forces). (b)  $\text{CS}_2$  (greater dispersion forces). (c)  $\text{Cl}_2$  (greater dispersion forces). (d) LiF (ionic compound). (e)  $\text{NH}_3$  (hydrogen bond).

**12.18** (a) Hydrogen bonding, dispersion forces. (b) Dispersion forces. (c) Dispersion forces. (d) The attractive forces of the covalent bond. **12.20** The compound on the left can form hydrogen bonds with itself (intramolecular hydrogen bonding). **12.32** Its viscosity is between that of ethanol and glycerol. **12.36** Ionic.

**12.38** Covalent. **12.40** Li: metallic; Be: metallic; B: molecular (An elemental form of boron is  $\text{B}_{12}$ ); C: covalent; N: molecular; O: (molecular); F: molecular; Ne: (atomic). **12.42** Covalent: Si, C. Molecular:  $\text{Se}_8$ ,  $\text{HBr}$ ,  $\text{CO}_2$ ,  $\text{P}_4\text{O}_6$ ,  $\text{SiH}_4$ . **12.44** Simple cubic: one sphere; body-centered cubic: two spheres; face-centered cubic: four spheres. **12.46**  $6.20 \times 10^{23}$  atom/mol. **12.48** 458 pm.

**12.50**  $\text{XY}_3$ . **12.52** Each C atom in diamond is covalently bonded to four other C atoms. Graphite has delocalized electrons.

**12.72** 2670 kJ. **12.74** 47.03 kJ/mol. **12.76** First step: freezing; second step: sublimation. **12.78** Additional heat is liberated when steam condenses at  $100^\circ\text{C}$ . **12.80** 331 mmHg. **12.84** The pressure exerted by the blades on the ice lowers the m.p. of the ice. A film

of liquid water between the blades and the ice provides lubrication for the movement of the skater. **12.86** (a) Water will boil and turn into steam. (b) Water vapor will turn into ice. (c) Liquid water will vaporize. **12.88** (a) Dispersion and hydrogen bonding.

(b) Dispersion. (c) Ionic, hydrogen bonding (in HF), dispersion. (d) Metallic bond. **12.90** HF molecules form hydrogen bonds; HI molecules do not. **12.92** (a) Solid. (b) Vapor. **12.94** The critical temperature of CO<sub>2</sub> is 31°C. The liquid CO<sub>2</sub> in the fire extinguisher is converted to critical fluid on a hot summer day. **12.96** Initially water boils under reduced pressure. During boiling, water cools and it freezes. Eventually it sublimes. **12.98** (a) Two. (b) Diamond. (c) Apply high pressure and high temperature. **12.100** W: Au; X: PbS; Y: I<sub>2</sub>; Z: SiO<sub>2</sub>. **12.102**  $8.3 \times 10^{-3}$  atm. **12.104** Smaller ions have high charge density and are more effective in ion-dipole interaction. **12.106** 3Hg + O<sub>3</sub> → 3HgO. Conversion to solid HgO changes its surface tension. **12.108** 66.8%. **12.110** 1.69 g/cm<sup>3</sup>. **12.112** When water freezes, the heat released protects the fruits. Also, the ice forms help to insulate the fruits by keeping the temperature at 0°C. **12.114** The water vapor generated from the combustion of methane condenses on the cold beaker outside. **12.116** The ice condenses the water vapor inside. Because the water is still hot, it will begin to boil at reduced pressure. (Air must first be driven off in the beginning.) **12.118**  $6.019 \times 10^{23}$  Fe atoms/mol. **12.120** Na.

## Chapter 13

**13.8** Cyclohexane cannot form hydrogen bonds with ethanol.

**13.10** The longer the chain gets, the more nonpolar the molecule becomes. The —OH group can form hydrogen bonds with water, but the rest of the molecule cannot. **13.14** (a) 25.9 g. (b)  $1.72 \times 10^3$  g. **13.16** (a) 2.68 m. (b) 7.82 m. **13.20**  $5.0 \times 10^2$  m; 18.3 M. **13.22** (a) 2.41 m. (b) 2.13 M. (c) 0.0587 L. **13.26** 45.9 g.

**13.32** Oxygen gas was driven off by boiling. **13.34** At the bottom of the mine, the carbon dioxide pressure is greater and the dissolved gas is not released from the solution. Coming up, the pressure decreases and carbon dioxide is released from the solution. **13.36** 0.28 L. **13.50**  $1.3 \times 10^3$  g. **13.52** Ethanol: 30.0 mmHg; propanol: 26.3 mmHg. **13.54** 128 g. **13.56** 0.59 m.

**13.58** 120 g/mol; C<sub>4</sub>H<sub>8</sub>O<sub>4</sub>. **13.60** –8.6°C. **13.62** 4.3 × 10<sup>2</sup> g/mol; C<sub>24</sub>H<sub>20</sub>P<sub>4</sub>. **13.64**  $1.75 \times 10^4$  g/mol. **13.66** 343 g/mol. **13.72**

Boiling point, vapor pressure, osmotic pressure. **13.74** (b) > (c) > (a). **13.76** 0.9420 m. **13.78** 7.6 atm. **13.80** 1.6 atm. **13.82** 3.5 atm. **13.84** (a) 104 mmHg. (b) 116 mmHg. **13.86**  $2.95 \times 10^3$  g/mol.

**13.88** No. Compound is assumed to be pure, monomeric, and a nonelectrolyte. **13.90** 12.3 M. **13.92** Soln A: 124 g/mol; Soln B: 248 g/mol. Dimerization in benzene. **13.94** (a) Boiling under reduced pressure. (b) CO<sub>2</sub> boils off, expands, and cools, condensing water vapor to form fog. **13.96** (a) Seawater contains many solutes. (b) Solubility of CO<sub>2</sub> in water decreases at reduced pressure.

(c) Density of solution is close to that of water. (d) Molality is independent of temperature. (e) Methanol is volatile. **13.98** C<sub>6</sub>H<sub>12</sub>: 36%; C<sub>10</sub>H<sub>8</sub>: 65%. **13.100** First row: positive, positive; second row: A ↔ A, B ↔ B < A ↔ B, negative; third row: A ↔ A, B ↔ B = A ↔ B, no deviation. **13.102** Ethanol and water have an intermolecular attraction that results in an overall smaller volume.

**13.104** 14.2%. **13.106** (a)  $X_A = 0.524$ ,  $X_B = 0.476$ . (b)  $P_A = 50$  mmHg,  $P_B = 20$  mmHg. (c)  $P_A = 67$  mmHg,  $P_B = 12$  mmHg. **13.108** A:  $1.9 \times 10^2$  mmHg; B:  $4.0 \times 10^2$  mmHg. **13.110** –0.737°C.

## Chapter 14

**14.6** (a) 0.049 M/s. (b) –0.025 M/s. **14.16** (a) Rate =  $k[F_2][ClO_2]$ . (b)  $1.2/M \cdot s$ . (c)  $2.4 \times 10^{-4} M/s$ . **14.18** (a) Rate =  $k[X]^2[Y]^3$ ;

fifth order. (b)  $0.68 M/s$ . **14.20** (a)  $0.046 s^{-1}$ . (b)  $0.13 M^{-1} s^{-1}$ .

**14.22** Three half-lives or  $2.08/k$ . **14.24** (a)  $0.0198 s^{-1}$ . (b) 151 s.

**14.26** (a) 3.6 s. (b) 3.0 s, 6.6 s. **14.34** 135 kJ/mol. **14.36** 371°C.

**14.38** 51.0 kJ/mol. **14.48** (a) Rate =  $k[X_2][Y]$ . (b) Z does not appear in the rate-determining step. (c)  $X_2 + Y \longrightarrow XY + X$  (slow);  $X + Z \longrightarrow XZ$  (fast). **14.56** Rate =  $(k_1 k_2 / k_{-1})[E][S]$ .

**14.58** Temperature, activation energy, concentration of reactant, catalyst. **14.60** Area of large sphere: 22.6 cm<sup>2</sup>; area of eight small spheres: 44.9 cm<sup>2</sup>. The sphere with the larger surface area is the more effective catalyst. **14.62** [H<sub>2</sub>O] can be treated as a constant.

**14.64** (a) Rate =  $k[H^+][CH_3COCH_3]$ . (b)  $3.8 \times 10^{-3}/M \cdot s$ .

**14.66** 2.63 atm. **14.68**  $M^{-2} s^{-1}$ . **14.70** 56.4 min. **14.72** (b), (d), and (e). **14.74** 0.098%. **14.76** (a) Increased. (b) Decreased. (c) Decreased. (d) Increased. **14.78** 0.0896 min<sup>-1</sup>. **14.80**  $1.12 \times 10^3$  min.

**14.82** (a) Rate =  $k[X][Y]^2$ . (b)  $1.9 \times 10^{-2} M^{-2} s^{-1}$ . **14.84** 3.1.

**14.86** During the first 10 min or so the engine is relatively cold so the reaction will be slow. **14.90** At very high H<sub>2</sub> concentration, rate =  $(k_1/k_2)[NO]^2$ , at very low H<sub>2</sub> concentration, rate =  $k_1[NO]^2[H_2]$ . **14.92** NO<sub>2</sub> + NO<sub>2</sub> → NO<sub>3</sub> + NO (slow); NO<sub>3</sub> + CO → NO<sub>2</sub> + CO<sub>2</sub> (fast). **14.94** At high pressures, all the sites on W are occupied so the rate is zero order in [PH<sub>3</sub>].

**14.96** (a)  $\Delta[B]/\Delta t = k_1[A] - k_2[B]$ . (b) [B] =  $(k_1/k_2)[A]$ . **14.98** Use H<sub>2</sub>O enriched with the <sup>18</sup>O isotope. Only mechanism (a) would give acetic acid with that isotope and only mechanism (b) would give methanol with that isotope. **14.100** (1) (b) < (c) < (a). (2) (a): –40 kJ/mol; (b): 20 kJ/mol; (c): –20 kJ/mol. **14.102** Ti acts as a catalyst to decompose steam to form the flammable H<sub>2</sub> gas.

**14.104** (a)  $2.5 \times 10^{-5} M/s$ . (b)  $2.5 \times 10^{-5} M/s$ . (c)  $8.3 \times 10^{-6} M$ .

**14.106** (a) Drinking too much alcohol means all the active sites of the enzyme are occupied and the excess alcohol will damage the central nervous system. (b) Both ethanol and methanol will compete for the same active site of the enzyme, leading to methanol's discharge from the body. **14.108**  $t_{\frac{1}{2}} = C(1/[A]_0^{n-1})$ . Substituting  $n = 0, 1$ , and 2 for zero-, first-, and second-order reactions. **14.110** Second order.  $0.42/M \cdot \text{min}$ . **14.112** (d).

## Chapter 15

**15.8** (a)  $K_p = P_{CO_2}P_{H_2}$ . (b)  $K_p = P_{SO_2}^2P_{O_2}$ . **15.12** (a) A + C ⇌ AC. (b) A + D ⇌ AD. **15.14**  $1.08 \times 10^7$ . **15.16**  $1.1 \times 10^{-5}$ .

**15.18** (a) 0.082. (b) 0.29. **15.20** 0.105;  $2.05 \times 10^{-3}$ . **15.22**  $7.09 \times 10^{-3}$ . **15.24** 3.3. **15.26** 0.0353. **15.30** [N<sub>2</sub>] and [H<sub>2</sub>] will decrease and [NH<sub>3</sub>] will increase. **15.32** 0.50 atm and 0.020 atm. **15.34** [I] =  $8.58 \times 10^{-4} M$ ; [I<sub>2</sub>] = 0.0194 M. **15.36** (a) 0.52. (b) [CO<sub>2</sub>] = 0.48 M; [H<sub>2</sub>] = 0.020 M; [CO] = 0.075 M; [H<sub>2</sub>O] = 0.065 M.

**15.38** [H<sub>2</sub>] = [CO<sub>2</sub>] = 0.05 M; [H<sub>2</sub>O] = [CO] = 0.11 M.

**15.44** (a) Shift to the right. (b) No effect. (c) No effect.

**15.46** (a) No effect. (b) No effect. (c) Shift to the left. (d) No effect. (e) Shift to the left. **15.48** (a) Shift to the right. (b) Shift to the left. (c) Shift to the right. (d) Shift to the left. (e) No effect.

**15.50** No change. **15.52** (a) Shift to the right. (b) No effect. (c) No effect. (d) Shift to the left. (e) Shift to the right. (f) Shift to the left. (g) Shift to the right. **15.54** (a) NO: 0.24 atm; Cl<sub>2</sub>: 0.12 atm.

(b) 0.017. **15.56** (a) No. (b) Yes. **15.58** (a)  $8 \times 10^{-44}$ . (b) The reaction needs an input of energy to get started. **15.60** (a) 1.7.

(b)  $P_A = 0.69$  atm;  $P_B = 0.81$  atm. **15.62**  $1.5 \times 10^5$ . **15.64** H<sub>2</sub>:

0.28 atm; Cl<sub>2</sub>: 0.049 atm; HCl: 1.67 atm. **15.66** 50 atm. **15.68**  $3.84 \times 10^{-2}$ . **15.70** 3.13. **15.72** N<sub>2</sub>: 0.860 atm; H<sub>2</sub>: 0.366 atm; NH<sub>3</sub>:  $4.40 \times 10^{-3}$  atm. **15.74** (a) 1.16. (b) 53.7%. **15.76** (a) 0.49. (b) 0.23.

(c) 0.037. (d) 0.037 mol. **15.78** [H<sub>2</sub>] = 0.070 M; [I<sub>2</sub>] = 0.182 M; [HI] = 0.825 M. **15.80** (c). **15.82** (a) Color deepens. (b) Increases. (c) Decreases. (d) Increases. (e) Unchanged. **15.84** K is more volatile than Na. Therefore, its removal shifts the equilibrium to

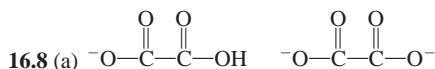
the right. **15.86** (a) High temperature and low pressure. (b) (i)  $1.4 \times 10^5$ ; (ii)  $\text{CH}_4$ ;  $\text{H}_2\text{O}$ : 2 atm;  $\text{CO}$ : 13 atm;  $\text{H}_2$ : 39 atm. **15.88** 1.2.

**15.90** (a) React Ni with CO above  $50^\circ\text{C}$ . (b) The decomposition is endothermic. Heat  $\text{Ni}(\text{CO})_4$  above  $200^\circ\text{C}$ . **15.92** (a)  $K_P = 2.6 \times 10^{-6}$ ;  $K_c = 1.1 \times 10^{-7}$ . (b) 2.2 g; 22 mg/m<sup>3</sup>; yes. **15.94**  $[\text{NH}_3] = 0.042 \text{ M}$ ;  $[\text{N}_2] = 0.086 \text{ M}$ ;  $[\text{H}_2] = 0.26 \text{ M}$ . **15.96**  $[\text{N}_2\text{O}_4] = 0.996 \text{ M}$ ,  $[\text{NO}_2] = 0.0678 \text{ M}$ . The color will be darker. **15.98** (a) Assuming  $\Delta H^\circ > 0$  and  $T_2 > T_1$ , the equation predicts that  $K_2 > K_1$ , according to Le Châtelier's principle. (b) 43.4 kJ/mol. **15.100** 4.0.

## Chapter 16

**16.4** (a) Nitrite ion:  $\text{NO}_2^-$ . (b) Hydrogen sulfate ion:  $\text{HSO}_4^-$ .

(c) Hydrogen sulfide ion:  $\text{HS}^-$ . (d) Cyanide ion:  $\text{CN}^-$ . (e) Formate ion:  $\text{HCOO}^-$ . **16.6** (a)  $\text{H}_2\text{S}$ . (b)  $\text{H}_2\text{CO}_3$ . (c)  $\text{HCO}_3^-$ . (d)  $\text{H}_3\text{PO}_4$ . (e)  $\text{H}_2\text{PO}_4^-$ . (f)  $\text{HPO}_4^{2-}$ . (g)  $\text{H}_2\text{SO}_4$ . (h)  $\text{HSO}_4^-$ . (i)  $\text{HNO}_2$ . (j)  $\text{HSO}_3^-$ .



(b) Acid:  $\text{H}^+$  and  $\text{H}_2\text{C}_2\text{O}_4$ ; base:  $\text{C}_2\text{O}_4^{2-}$ ; both acid and base:  $\text{HC}_2\text{O}_4^-$ . **16.16** (a)  $6.3 \times 10^{-6} \text{ M}$ . (b)  $1.0 \times 10^{-16} \text{ M}$ . (c)  $2.7 \times 10^{-6} \text{ M}$ . **16.18** 6.72. **16.20** (a) Acidic. (b) Neutral. (c) Basic.

**16.22**  $1.98 \times 10^{-3} \text{ mol}$ ; 0.444. **16.24**  $2.2 \times 10^{-3} \text{ g}$ . **16.30** (1) (c). (2) (b) and (d). **16.32** (a) Strong base. (b) Weak base. (c) Weak base. (d) Weak base. (e) Strong base. **16.34** (a) False. (b) True. (c) True. (d) False. **16.36** To the left. **16.42**  $[\text{H}^+] = [\text{CH}_3\text{COO}^-] = 5.8 \times 10^{-4} \text{ M}$ ;  $[\text{CH}_3\text{COOH}] = 0.0181 \text{ M}$ . **16.44**  $2.3 \times 10^{-3} \text{ M}$ .

**16.46** (a) 3.5%. (b) 9.0%. (c) 33%. (d) 79%. Extent of ionization increases with dilution. **16.48** (a) 3.9%. (b) 0.30%. **16.52**  $[\text{H}^+] = [\text{HCO}_3^-] = 1.0 \times 10^{-4} \text{ M}$ ;  $[\text{CO}_3^{2-}] = 4.8 \times 10^{-11} \text{ M}$ . **16.56**  $7.1 \times 10^{-7}$ . **16.58** 1.5%. **16.62** (a)  $\text{H}_2\text{SO}_4 > \text{H}_2\text{SeO}_4$ . (b)  $\text{H}_3\text{PO}_4 > \text{H}_3\text{AsO}_4$ . **16.64** Only the anion of phenol can be stabilized by resonance. **16.72**  $\text{HZ} < \text{HY} < \text{HX}$ . **16.74** 4.82. **16.76**  $> 7$ .

**16.80**  $\text{AlCl}_3$  is a Lewis acid,  $\text{Cl}^-$  is a Lewis base. **16.82**  $\text{CO}_2$  and  $\text{BF}_3$ . **16.84** 0.106 L. **16.86** No. **16.88** No. **16.90**  $\text{CrO}$  is ionic and basic;  $\text{CrO}_3$  is covalent and acidic. **16.92**  $4.0 \times 10^{-2}$ . **16.94** 0.028.

**16.96**  $[\text{Na}^+] = 0.200 \text{ M}$ ;  $[\text{HCO}_3^-] = 4.6 \times 10^{-3} \text{ M}$ ;  $[\text{H}_2\text{CO}_3] = 2.4 \times 10^{-8} \text{ M}$ ;  $[\text{OH}^-] = 4.6 \times 10^{-3} \text{ M}$ ;  $[\text{H}^+] = 2.2 \times 10^{-12} \text{ M}$ .

**16.98**  $\text{NaCN} + \text{HCl} \longrightarrow \text{NaCl} + \text{HCN}$ . HCN is a very

weak acid so it escapes into the vapor phase. **16.100** 1.000.

**16.102** (a) Increases. (b) Decreases. (c) No effect. (d) Increases.

**16.104**  $1.6 \times 10^{-4}$ . **16.106** 4.40. **16.108**  $\text{NH}_3$ . **16.110** 21 mL.

**16.112**  $[\text{H}^+] = [\text{H}_2\text{PO}_4^-] = 0.0239 \text{ M}$ ;  $[\text{H}_3\text{PO}_4] = 0.076 \text{ M}$ ;  $[\text{HPO}_4^{2-}] = 6.2 \times 10^{-8} \text{ M}$ ;  $[\text{PO}_4^{3-}] = 1.2 \times 10^{-18} \text{ M}$ .

**16.114** (a)  $\text{Fe}_2\text{O}_3(s) + 6\text{HCl}(aq) \longrightarrow 2\text{FeCl}_3(aq) + 3\text{H}_2\text{O}(l)$ ;  $\text{Fe}_2\text{O}_3(s) + 6\text{H}^+(aq) \longrightarrow 2\text{Fe}^{3+}(aq) + 3\text{H}_2\text{O}(l)$ . (b) First stage:

$\text{CaCO}_3(s) + \text{HCl}(aq) \longrightarrow \text{Ca}^{2+}(aq) + \text{HCO}_3^-(aq) + \text{Cl}^-(aq)$ .

Second stage:  $\text{HCl}(aq) + \text{HCO}_3^-(aq) \longrightarrow \text{CO}_2(g) + \text{Cl}^-(aq) + \text{H}_2\text{O}(l)$ . Overall:  $\text{CaCO}_3(s) + 2\text{HCl}(aq) \longrightarrow \text{CaCl}_2(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$ . (c)  $-0.64$ . **16.116** Mg. **16.118** pH = 1.57.  $[\text{CN}^-] = 1.8 \times 10^{-8} \text{ M}$ .  $[\text{CN}^-] = 2.2 \times 10^{-5} \text{ M}$ .  $[\text{CN}^-]$  is greater in 1.00 M HCN solution as predicted by Le Châtelier's principle.

**16.120** 6.02.

## Chapter 17

**17.6** (a) and (c). **17.8** 4.74; (a) Higher concentration. **17.10** 7.03.

**17.12** 10; more effective against an added acid. **17.14** (a) 4.82.

(b) 4.64. **17.16** HC.  $pK_a$  is closest to pH. **17.18** 90.1 g/mol.

**17.20** (a) 110 g/mol. (b)  $1.6 \times 10^{-6}$ . **17.24** The atmospheric  $\text{CO}_2$  is converted to  $\text{H}_2\text{CO}_3$ , which neutralizes the NaOH. **17.26** Red.

**17.34** (a)  $7.8 \times 10^{-10}$ . (b)  $1.8 \times 10^{-18}$ . **17.36**  $2.6 \times 10^{-6} \text{ M}$ .

**17.38**  $1.7 \times 10^{-2} \text{ g/L}$ . **17.40**  $2.3 \times 10^{-9}$ . **17.42**  $[\text{NO}_3^-] = 0.076 \text{ M}$ ;  $[\text{Na}^+] = 0.045 \text{ M}$ ;  $[\text{Sr}^{2+}] = 1.6 \times 10^{-2} \text{ M}$ ;  $[\text{F}^-] = 1.1 \times 10^{-4} \text{ M}$ .

**17.46** (a) 0.013 M. (b)  $2.2 \times 10^{-4} \text{ M}$ . (c)  $3.3 \times 10^{-3} \text{ M}$ .

**17.48** (a)  $1.0 \times 10^{-5} \text{ M}$ . (b)  $1.1 \times 10^{-10} \text{ M}$ . **17.52** Complex ion formations. (a)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ . (b)  $[\text{Ag}(\text{CN})_2]^-$ . (c)  $[\text{HgCl}_4]^{2-}$ . For equations for the formation of the complex ions see Table 17.4.

**17.54**  $[\text{Cd}^{2+}] = 1.1 \times 10^{-18} \text{ M}$ ;  $[\text{Cd}(\text{CN})_4]^{2-} = 4.2 \times 10^{-3} \text{ M}$ ;  $[\text{CN}^-] = 0.48 \text{ M}$ . **17.56**  $3.5 \times 10^{-5} \text{ M}$ . **17.60** 0.011 M.

**17.62** Chloride ions will only precipitate  $\text{Ag}^+$  ions, or a flame test for  $\text{Cu}^{2+}$  ions. **17.64** (a) 1.37. (b) 5.28. (c) 8.85. **17.66** 2.51–4.41.

**17.68** 1.28 M. **17.70**  $[\text{H}^+] = 3.0 \times 10^{-13} \text{ M}$ ;  $[\text{CH}_3\text{COO}^-] = 0.050 \text{ M}$ ;  $[\text{CH}_3\text{COOH}] = 8.4 \times 10^{-10} \text{ M}$ ;  $[\text{OH}^-] = 0.0335 \text{ M}$ ;  $[\text{Na}^+] = 0.0835 \text{ M}$ . **17.72** 9.25; 9.18. **17.74** 9.97 g; 13.04.

**17.76**  $[\text{Ag}^+] = 2.0 \times 10^{-9} \text{ M}$ ;  $[\text{Cl}^-] = 0.080 \text{ M}$ ;  $[\text{Zn}^{2+}] = 0.070 \text{ M}$ ;  $[\text{NO}_3^-] = 0.060 \text{ M}$ . **17.78** pH is greater than 2.68 but less than 8.11.

**17.80** All except (a). **17.82**  $2.4 \times 10^{-13}$ . **17.84** A precipitate of  $\text{Fe}(\text{OH})_2$  will form. **17.86** The original precipitate is  $\text{HgI}_2$ . At higher concentration of KI, the complex ion  $\text{HgI}_4^{2-}$  forms so mass of  $\text{HgI}_2$  decreases. **17.88** 7.82–10.38. **17.90** (a)  $\text{AgI}$ . (b)  $1.6 \times 10^{-7} \text{ M}$ .

(c) 0.0016%. **17.92** (a)  $\text{MCO}_3 + 2\text{HCl} \longrightarrow \text{MCl}_2 + \text{H}_2\text{O} + \text{CO}_2$ ,  $\text{HCl} + \text{NaOH} \longrightarrow \text{NaCl} + \text{H}_2\text{O}$ . (b) 197 g/mol; Ba. **17.94** 2.

**17.96** (a) Sulfate. (b) Sulfide. (c) Iodide. **17.98** 13 mL. **17.100** (c).

**17.102** (a)  $1.7 \times 10^{-7} \text{ M}$ . (b) Because  $\text{MgCO}_3$  is fairly soluble.

(c) 12.40. (d)  $1.9 \times 10^{-8} \text{ M}$ . (e)  $\text{Ca}^{2+}$  because it is present in larger amounts. **17.106** At pH = 1.0:  $^+\text{NH}_3-\text{CH}_2-\text{COOH}$ ; at pH = 7.0:  $^+\text{NH}_3-\text{CH}_2-\text{COO}^-$ ; at pH = 12.0:  $\text{NH}_2-\text{CH}_2-\text{COO}^-$ . **17.108** 4.75. **17.110**  $6.2 \times 10^{-12}$ .

## Chapter 18

**18.6**  $8 \times 10^{-31}$ . The probability is practically zero for 1 mole of molecules. **18.10** (c)  $<$  (d)  $<$  (e)  $<$  (a)  $<$  (b). Solids have smaller entropies than gases. More complex structures have higher entropies.

**18.12** (a) 47.5 J/K · mol. (b)  $-12.5 \text{ J/K} \cdot \text{mol}$ . (c)  $-242.8 \text{ J/K} \cdot \text{mol}$ .

**18.14** (a)  $\Delta S < 0$ . (b)  $\Delta S > 0$ . (c)  $\Delta S > 0$ . (d)  $\Delta S < 0$ .

**18.18** (a)  $-1139 \text{ kJ/mol}$ . (b)  $-140.0 \text{ kJ/mol}$  (c)  $-2935.0 \text{ kJ/mol}$

**18.20** (a) At all temperatures. (b) Below 111 K. **18.24**  $8.0 \times 10^1 \text{ kJ/mol}$ . **18.26**  $4.572 \times 10^2 \text{ kJ/mol}$ ;  $4.5 \times 10^{-81}$ .

**18.28** (a)  $-24.6 \text{ kJ/mol}$ . (b)  $-1.10 \text{ kJ/mol}$ . **18.30**  $-341 \text{ kJ/mol}$ .

**18.32**  $-2.87 \text{ kJ/mol}$ . The process has a high activation energy.

**18.36**  $1 \times 10^3$ ; glucose + ATP  $\longrightarrow$  glucose 6-phosphate + ADP.

**18.38** (a) 0. (b)  $4.0 \times 10^4 \text{ J/mol}$ . (c)  $-3.2 \times 10^4 \text{ J/mol}$ . (d)  $6.4 \times 10^4 \text{ J/mol}$ . **18.40** (a) No reaction is possible because  $\Delta G > 0$ .

(b) The reaction has a very large activation energy and therefore a slow rate. (c) Reactants and products already at their equilibrium concentrations. **18.42** In all cases,  $\Delta H > 0$  and  $\Delta S > 0$ .  $\Delta G < 0$  for (a),  $= 0$  for (b), and  $> 0$  for (c). **18.44**  $\Delta S > 0$ . **18.46** (a) Most liquids have similar structure so the changes in entropy from liquid to vapor are similar. (b)  $\Delta S_{\text{vap}}$  are larger for ethanol and water because of hydrogen bonding (there are fewer microstates in these liquids). **18.48** (a)  $2\text{CO} + 2\text{NO} \longrightarrow 2\text{CO}_2 + \text{N}_2$ . (b) Oxidizing agent: NO; reducing agent: CO. (c)  $1 \times 10^{121}$ . (d)  $1.2 \times 10^{18}$ ; From left to right. (e) No. **18.50**  $2.6 \times 10^{-9}$ . **18.52** 976 K.

**18.54**  $\Delta S < 0$ ;  $\Delta H < 0$ . **18.56** 55 J/K · mol. **18.58** Increase in entropy of the surroundings offsets the decrease in entropy of the system. **18.60** 56 J/K. **18.62**  $4.5 \times 10^5$ . **18.64**  $4.5 \times 10^{-75}$  atm.

**18.66** (a) True. (b) True. (c) False. **18.68**  $\text{C} + \text{CuO} \rightleftharpoons \text{CO} + \text{Cu}$ ; 6.1. **18.70** Crystal structure has disorder or impurity.

**18.72** (a)  $7.6 \times 10^{14}$ . (b)  $4.1 \times 10^{-12}$ . **18.74** (a) A reverse disproportionation reaction. (b)  $8.2 \times 10^{15}$ . Yes, a large  $K$  makes this an efficient process. (c) Less effective. **18.76**  $1.8 \times 10^{70}$ .

Reaction has a large activation energy. **18.78** Heating the ore alone is not a feasible process.  $-214.3 \text{ kJ/mol}$ . **18.80**  $K_P = 36$ ; 981 K.

No. **18.82**  $X_{\text{CO}} = 0.45$ ;  $X_{\text{CO}_2} = 0.55$ . Use  $\Delta G_f^\circ$  values at 25°C

for 900°C. **18.84** 249 J/K. **18.86**  $3 \times 10^{-13}$  s. **18.88**  $\Delta S_{\text{sys}} = -327 \text{ J/K} \cdot \text{mol}$ ;  $\Delta S_{\text{surr}} = 1918 \text{ J/K} \cdot \text{mol}$ ;  $\Delta S_{\text{univ}} = 1591 \text{ J/K} \cdot \text{mol}$ . **18.90** *q*, *w*: **18.92**  $\Delta H < 0$ ;  $\Delta S < 0$ ;  $\Delta G < 0$ . **18.94** (a)  $\Delta H > 0$  (endothermic) and  $\Delta G < 0$  (spontaneous). Therefore,  $\Delta S > 0$ . (b) The rubber molecules become more entangled (resulting in a greater number of microstates) upon contraction. **18.96** Analogy is inappropriate. Entropy is a measure of the dispersal of molecules among available energy levels. The entropy of the room is the same whether it is tidy or not. **18.98**  $\Delta G^\circ = 62.5 \text{ kJ/mol}$ ;  $\Delta H^\circ = 157.8 \text{ kJ/mol}$ ;  $\Delta S^\circ = 109 \text{ J/K} \cdot \text{mol}$ .

## Chapter 19

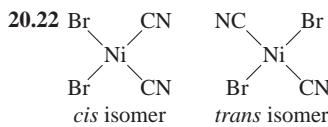
- 19.2** (a)  $\text{Mn}^{2+} + \text{H}_2\text{O}_2 + 2\text{OH}^- \longrightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$ .  
 (b)  $2\text{Bi}(\text{OH})_3 + 3\text{SnO}_2^{2-} \longrightarrow 2\text{Bi} + 3\text{H}_2\text{O} + 3\text{SnO}_3^{2-}$ .  
 (c)  $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 3\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{Cr}^{3+} + 6\text{CO}_2 + 7\text{H}_2\text{O}$ .  
 (d)  $2\text{Cl}^- + 2\text{ClO}_3^- + 4\text{H}^+ \longrightarrow \text{Cl}_2 + 2\text{ClO}_2 + 2\text{H}_2\text{O}$ .
- 19.12** 2.46 V;  $\text{Al} + 3\text{Ag}^+ \longrightarrow 3\text{Ag} + \text{Al}^{3+}$ . **19.14**  $\text{Cl}_2(g)$  and  $\text{MnO}_4^-(aq)$ . **19.16** Only (a) and (d) are spontaneous. **19.18** (a) Li. (b)  $\text{H}_2$ . (c)  $\text{Fe}^{2+}$ . (d)  $\text{Br}^-$ . **19.22** 0.368 V. **19.24** (a)  $-432 \text{ kJ/mol}$ ;  $5 \times 10^{75}$ . (b)  $-104 \text{ kJ/mol}$ ;  $2 \times 10^{18}$ . (c)  $-178 \text{ kJ/mol}$ ;  $1 \times 10^{31}$ . (d)  $-1.27 \times 10^3 \text{ kJ/mol}$ ;  $8 \times 10^{21}$ . **19.26** 0.37 V;  $-36 \text{ kJ/mol}$ ;  $2 \times 10^6$ . **19.30** (a) 2.23 V; 2.23 V;  $-430 \text{ kJ/mol}$ . (b) 0.02 V; 0.04 V;  $-23 \text{ kJ/mol}$ . **19.32** 0.083 V. **19.34** 0.010 V. **19.38** 1.09 V. **19.46** (a) anode:  $2\text{Cl}^-(aq) \longrightarrow \text{Cl}_2(g) + 2e^-$ , cathode:  $\text{Ba}^{2+}(aq) + 2e^- \longrightarrow \text{Ba}(s)$ . (b) 0.64 g. **19.48** (a)  $\$2.10 \times 10^3$ . (b)  $\$2.46 \times 10^3$ . (c)  $\$4.70 \times 10^3$ . **19.50** (a) 0.14 F. (b) 0.121 F. (c) 0.10 F. **19.52** (a)  $\text{Ag}^+ + e^- \longrightarrow \text{Ag}$ . (b)  $2\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$ . (c)  $6.0 \times 10^2 \text{ C}$ . **19.54** (a) 0.589 g Cu. (b) 0.133 A. **19.56** 2.3 h. **19.58**  $9.66 \times 10^4 \text{ C}$ . **19.60** 0.0710 F. **19.62** 0.156 M;  $\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$ . **19.64** 45.1%. **19.66** (a)  $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$ . (b) 5.40%. **19.68** 0.231 mg  $\text{Ca}^{2+}/\text{mL}$  blood. **19.70** (a) 0.80 V. (b)  $2\text{Ag}^+ + \text{H}_2 \longrightarrow 2\text{Ag} + 2\text{H}^+$ . (c) (i) 0.92 V; (ii) 1.10 V. (d) The cell operates as a pH meter. **19.72** Fluorine gas reacts with water. **19.74**  $2.5 \times 10^2 \text{ h}$ . **19.76**  $\text{Hg}_2^{2+}$ . **19.78**  $[\text{Mg}^{2+}] = 0.0500 \text{ M}$ ,  $[\text{Ag}^+] = 7 \times 10^{-55} \text{ M}$ , 1.44 g. **19.80** (a) 0.206 L  $\text{H}_2$ . (b) 6.09  $\times 10^{23} \text{ mol } e^-$ . **19.82** (a)  $-1356.8 \text{ kJ/mol}$ . (b) 1.17 V. **19.84** +3. **19.86** 6.8 kJ/mol; 0.064. **19.88** 1.4 A. **19.90** +4. **19.92** 1.60  $\times 10^{-19} \text{ C/e}^-$ . **19.94** A cell made of  $\text{Li}^+/\text{Li}$  and  $\text{F}_2/\text{F}^-$  gives the maximum voltage of 5.92 V. Reactive oxidizing and reducing agents are hard to handle. **19.96**  $2 \times 10^{20}$ . **19.98** (a)  $E^\circ$  for X is negative;  $E^\circ$  for Y is positive. (b) 0.59 V. **19.100** (a) The reduction potential of  $\text{O}_2$  is insufficient to oxidize gold. (b) Yes. (c)  $2\text{Au} + 3\text{F}_2 \longrightarrow 2\text{AuF}_3$ . **19.102**  $[\text{Fe}^{2+}] = 0.0920 \text{ M}$ ,  $[\text{Fe}^{3+}] = 0.0680 \text{ M}$ . **19.104** (b) 104 A · h. The concentration of  $\text{H}_2\text{SO}_4$  keeps decreasing. (c) 2.01 V;  $-3.88 \times 10^5 \text{ J/mol}$ . **19.106** (a) Unchanged. (b) Unchanged. (c) Squared. (d) Doubled. (e) Doubled. **19.108** Stronger. **19.110**  $4.4 \times 10^2 \text{ atm}$ . **19.112** (a) 8.2 g. (b) 0.40 M. **19.114** (a) Anode (Mg):  $\text{Mg} \longrightarrow \text{Mg}^{2+} + 2e^-$  (also:  $\text{Mg} + 2\text{HCl} \longrightarrow \text{MgCl}_2 + \text{H}_2$ ). Cathode (Cu):  $2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$ . (b) The solution does not turn blue. (c)  $\text{Mg}(\text{OH})_2$ . **19.116** 2  $\times 10^{37}$ . **19.118** (a)  $9.83 \times 10^3 \text{ C}$ . (b) 21.7 min. (c) 2.97 g  $\text{Mg}(\text{OH})_2$ .

## Chapter 20

- 20.12** (a) +3. (b) 6. (c) Oxalate. **20.14** (a) Na: +1; Mo: +6. (b) Mg: +2; W: +6. (c) K: +1; Fe: +2. **20.16** (a) *cis*-dichlorobis(ethylenediamine)cobalt(III). (b) pentaamminechloroplatinum(IV) chloride. (c) hexaamminecobalt(III) chloride. (d) pentaamminechlorocobalt(III) chloride. (e) *trans*-diamminedichloroplatinum(II).

**20.18** (a)  $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$ . (b)  $\text{Fe}(\text{CO})_5$ . (c)  $\text{K}_2[\text{Cu}(\text{CN})_4]$ .

(d)  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ . **20.20** (a) 2. (b) 2.



**20.28**  $\text{CN}^-$  is a strong-field ligand. Absorption occurs near the high-energy end of the spectrum (blue) and the complex ion looks yellow.  $\text{H}_2\text{O}$  is a weaker-field ligand and absorption occurs in the orange or red part of the spectrum. Consequently, the complex ion appears green or blue. **20.30** (a) two unpaired spins. (b) four unpaired spins. **20.32** 2;  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ . **20.36** Use  $^{14}\text{CN}^-$  label (in  $\text{NaCN}$ ). **20.38** First  $\text{Cu}(\text{CN})_2$  (white) is formed. It redissolves as  $\text{Cu}(\text{CN})_4^{2-}$ . **20.40**  $1.4 \times 10^2$ . **20.42**  $6.7 \times 10^{13}$ . **20.44** The  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  ion is a high-spin complex, containing five unpaired spins. **20.46** These will absorb at longer wavelength:

(a)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ , (b)  $[\text{FeF}_6]^{3-}$ , (c)  $[\text{CuCl}_4]^{2-}$ . **20.48** (a)  $4\text{Au}(s) + 8\text{CN}^-(aq) + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \longrightarrow 4[\text{Au}(\text{CN})_2]^{-(aq)} + 4\text{OH}^-(aq)$ . (b)  $\text{Zn}(s) + 2[\text{Au}(\text{CN})_2]^{-(aq)} \longrightarrow [\text{Zn}(\text{CN})_4]^{2-}(aq) + 2\text{Au}(s)$ . (c) Linear (Au is *sp*-hybridized). **20.50**  $\text{Mn}^{3+}$  ( $3d^5$ ) because it is less stable than  $\text{Cr}^{3+}$  ( $3d^5$ ). **20.52** EDTA sequesters metal ions like  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  that are essential for bacterial growth and function. **20.54** 3. **20.56** I is the *cis* isomer and II is the *trans* isomer. **20.58**  $[\text{Ag}^+] = 2.2 \times 10^{-20} \text{ M}$ . **20.60** (a)  $2.7 \times 10^6$ . (b) Free  $\text{Cu}^+$  ions are unstable in solution. The only stable  $\text{Cu}(\text{I})$  compounds are insoluble. **20.62** (a) No. It is easily reduced to  $\text{Cu}^{2+}$ . (b) Potassium hexafluorocuprate(III). It is paramagnetic and has an octahedral geometry. (c) Diamagnetic.

## Chapter 21

- 21.6** (a)  ${}_{-1}^0\beta$ . (b)  ${}_{20}^0\text{Ca}$ . (c)  ${}_{-2}^4\alpha$ . (d)  ${}_{0n}^1$ . **21.14** (a)  ${}_{-3}^0\text{Li}$ . (b)  ${}_{11}^{25}\text{Na}$ . (c)  ${}_{21}^{48}\text{Sc}$ . **21.16** (a)  ${}_{10}^{17}\text{Ne}$ . (b)  ${}_{20}^{45}\text{Ca}$ . (c)  ${}_{-3}^{92}\text{Tc}$ . (d)  ${}_{-80}^{195}\text{Hg}$ . (e)  ${}_{-96}^{242}\text{Cm}$ . **21.18**  $6 \times 10^9 \text{ kg/s}$ . **21.20** (a)  $4.55 \times 10^{-12} \text{ J}$ ;  $1.14 \times 10^{-12} \text{ J/nucleon}$ . (b)  $2.36 \times 10^{-10} \text{ J}$ ;  $1.28 \times 10^{-12} \text{ J/nucleon}$ . **21.24**  $0.250 \text{ d}^{-1}$ ;  $2.77 \text{ d}$ . **21.26** 2.7 d. **21.28**  ${}_{-82}^{208}\text{Pb}$ . **21.30** A: 0; B: 0.25 mole; C: 0; D: 0.75 mole. **21.34** (a)  ${}_{-34}^{80}\text{Se} + {}_1^2\text{H} \longrightarrow {}_{-1}^1\text{p} + {}_{-34}^{81}\text{Se}$ . (b)  ${}_{-4}^{9}\text{Be} + {}_1^2\text{H} \longrightarrow {}_{-1}^2\text{p} + {}_{-3}^9\text{Li}$ . (c)  ${}_{-5}^{10}\text{B} + {}_0^1\text{n} \longrightarrow {}_{-4}^2\alpha + {}_{-3}^7\text{Li}$ . **21.36**  ${}_{-80}^{198}\text{Hg} + {}_{0n}^1 \longrightarrow {}_{-79}^{198}\text{Au} + {}_{-1}^1\text{p}$ . **21.48**  $\text{IO}_3^-$  is only formed from  $\text{IO}_4^-$ . **21.50** Incorporate  ${}^{59}\text{Fe}$  into a person's body. After a few days isolate red blood cells and monitor radioactivity from the hemoglobin molecules. **21.52** An analogous Pauli exclusion principle for nucleons. **21.54** (a) 0.343 mCi. (b)  ${}_{-93}^{237}\text{Np} \longrightarrow {}_{-4}^{2}\alpha + {}_{-91}^{233}\text{Pa}$ . **21.56** (a)  $1.040 \times 10^{-12} \text{ J/nucleon}$ . (b) 1.111  $\times 10^{-12} \text{ J/nucleon}$ . (c)  $1.199 \times 10^{-12} \text{ J/nucleon}$ . (d) 1.410  $\times 10^{-12} \text{ J/nucleon}$ . **21.58**  ${}_{-1}^{18}\text{N} \longrightarrow {}_{-8}^{18}\text{O} + {}_{-1}^0\beta$ . **21.60** Radioactive dating. **21.62** (a)  ${}_{-83}^{209}\text{Bi} + {}_{-2}^4\alpha \longrightarrow {}_{-85}^{211}\text{At} + {}_{-1}^2\text{n}$ . (b)  ${}_{-83}^{209}\text{Bi}(\alpha, 2n){}_{-85}^{211}\text{At}$ . **21.64** The sun exerts a much greater gravity on the particles. **21.66**  $2.77 \times 10^3 \text{ yr}$ . **21.68** (a)  ${}_{-19}^{40}\text{K} \longrightarrow {}_{-18}^{40}\text{Ar} + {}_{-1}^0\beta$ . (b)  $3.0 \times 10^9 \text{ yr}$ . **21.70** (a)  $5.59 \times 10^{-15} \text{ J}$ ;  $2.84 \times 10^{-13} \text{ J}$ . (b) 0.024 mol. (c)  $4.06 \times 10^6 \text{ kJ}$ . **21.72**  $2.7 \times 10^{14} {}_{-131}^{131}\text{I}$  atoms. **21.74**  $5.9 \times 10^{23} \text{ mol}$ . **21.76** All except gravitational. **21.78**  ${}_{-2}^{238}\text{U}$  and  ${}_{-2}^{232}\text{Th}$ . **21.80**  $8.3 \times 10^{-4} \text{ nm}$ . **21.82**  ${}_{-1}^3\text{H}$ . **21.84** The reflected neutrons induced a nuclear chain reaction. **21.86**  $2.1 \times 10^2 \text{ g/mol}$ . **21.88** Most of the hazards of a nuclear power plant are discussed in Section 21.5. However, it contributes much less to global warming than a coal-fired power plant. **21.90** (a)  ${}_{-94}^{238}\text{Pu} \longrightarrow {}_{-2}^4\text{He} + {}_{-92}^{234}\text{U}$ . (b)  $t = 0$ : 0.58 mW;  $t = 10 \text{ yr}$ : 0.53 mW. **21.92** 0.49 rem.

## Chapter 22

- 22.8**  $\text{---CH}_2\text{---CHCl---CH}_2\text{---CCl}_2\text{---}$ . **22.10** By an addition reaction involving styrene monomers. **22.12** (a)  $\text{CH}_2=\text{CH---CH=CH}_2$ .

(b) HO<sub>2</sub>C(CH<sub>2</sub>)<sub>6</sub>NH<sub>2</sub>. **22.22** At 35°C the enzyme begins to denature. **22.28** Proteins are made of 20 amino acids. Nucleic acids are made of only four building blocks (purines, pyrimidines, sugar, phosphate group). **22.30** C-G base pairs have three hydrogen bonds; A-T base pairs have two hydrogen bonds. The sample with the higher C-G pairs has the higher mpt. **22.32** Leg muscles are active, have a high metabolic rate and hence a high concentration of myoglobin. The iron content in Mb makes the meat look dark. **22.34** Insects have blood that contains no hemoglobin. It is unlikely that a human-sized insect could obtain sufficient oxygen for metabolism by diffusion. **22.36** There are four Fe atoms per hemoglobin molecule. **22.38** Mostly dispersion forces. **22.40** Gly-Ala-Phe-Glu-His-Gly-Ala-Leu-Val. **22.42** No.

Enzymes only act on one of the two enantiomers of a compound. **22.44** When deoxyhemoglobin binds to oxygen, there is a structural change due to the cooperativity effect, which causes the crystal to break up. Because myoglobin is made up of only one subunit, there is no structural change as deoxymyoglobin is converted to oxymyoglobin. **22.46** A sequence of only 2 bases to define a particular amino acid has a total of 4<sup>2</sup> or 16 possible combinations, not enough to cover the 20 amino acids. A sequence of 3 bases has 4<sup>3</sup> or 64 combinations, which are more than enough. **22.48** Yes, because  $\Delta G < 0$ . As temperature is lowered,  $\Delta G$  becomes less negative. The reaction becomes spontaneous in the reverse direction and eventually denaturation occurs.

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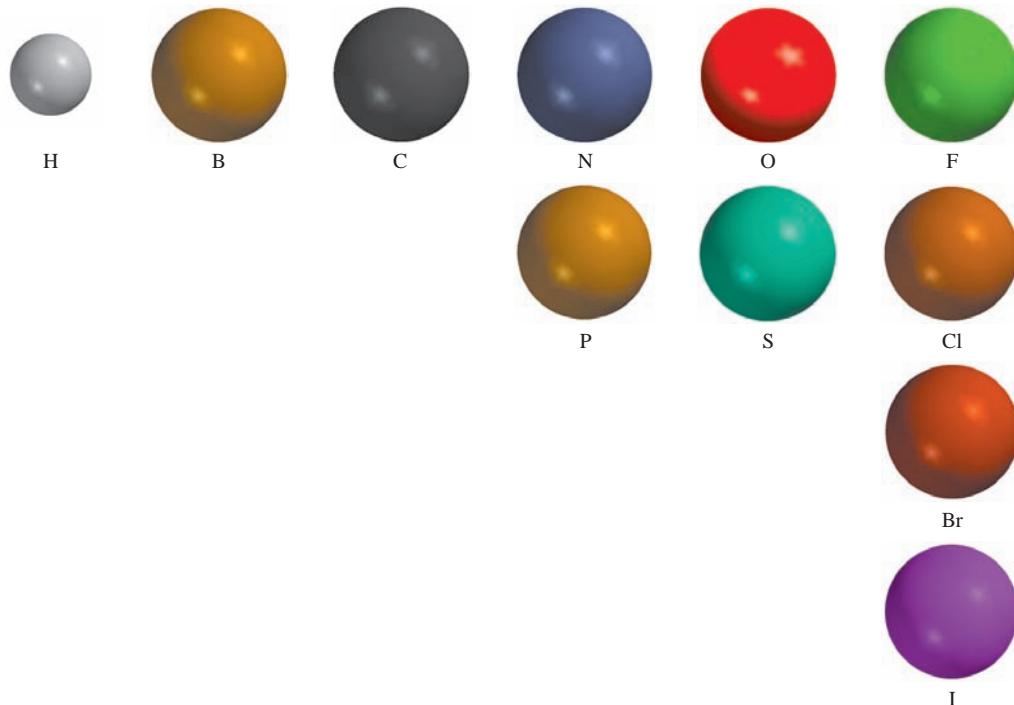
## Fundamental Constants

|                           |  |
|---------------------------|--|
| Avogadro's number         | $6.0221415 \times 10^{23}$   |
| Electron charge ( $e$ )   | $1.60217653 \times 10^{-19}\text{C}$   |
| Electron mass             | $9.1093826 \times 10^{-28}\text{ g}$   |
| Faraday constant ( $F$ )  | $96,485.3383\text{ C/mol }e^-$   |
| Gas constant ( $R$ )      | $8.314\text{ J/K} \cdot \text{mol}$ ( $0.08206\text{ L} \cdot \text{atm/K} \cdot \text{mol}$ ) |
| Planck's constant ( $h$ ) | $6.6260693 \times 10^{-34}\text{ J} \cdot \text{s}$  |
| Proton mass               | $1.672621 \times 10^{-24}\text{ g}$  |
| Neutron mass              | $1.67492728 \times 10^{-24}\text{ g}$  |
| Speed of light in vacuum  | $2.99792458 \times 10^8\text{ m/s}$  |

## Useful Conversion Factors and Relationships

$$\begin{aligned}1 \text{ lb} &= 453.6 \text{ g} \\1 \text{ in} &= 2.54 \text{ cm (exactly)} \\1 \text{ mi} &= 1.609 \text{ km} \\1 \text{ km} &= 0.6215 \text{ mi} \\1 \text{ pm} &= 1 \times 10^{-12} \text{ m} = 1 \times 10^{-10} \text{ cm} \\1 \text{ gal} &= 3.785 \text{ L} = 4 \text{ quarts} \\1 \text{ atm} &= 760 \text{ mmHg} = 760 \text{ torr} = 101,325 \text{ N/m}^2 = 101,325 \text{ Pa} \\1 \text{ cal} &= 4.184 \text{ J (exactly)} \\1 \text{ L atm} &= 101.325 \text{ J} \\1 \text{ J} &= 1 \text{ C} \times 1 \text{ V} \\?^\circ\text{C} &= (^\circ\text{F} - 32^\circ\text{F}) \times \frac{5^\circ\text{C}}{9^\circ\text{F}} \\?^\circ\text{F} &= \frac{9^\circ\text{F}}{5^\circ\text{C}} \times (^\circ\text{C}) + 32^\circ\text{F} \\?^\circ\text{K} &= (^\circ\text{C} + 273.15^\circ\text{C}) \left( \frac{1 \text{ K}}{1^\circ\text{C}} \right)\end{aligned}$$

Color Codes for Molecular Models



## Some Prefixes Used with SI Units

|          |           |                 |            |
|----------|-----------|-----------------|------------|
| tera (T) | $10^{12}$ | centi (c)       | $10^{-2}$  |
| giga (G) | $10^9$    | milli (m)       | $10^{-3}$  |
| mega (M) | $10^6$    | micro ( $\mu$ ) | $10^{-6}$  |
| kilo (k) | $10^3$    | nano (n)        | $10^{-9}$  |
| deci (d) | $10^{-1}$ | pico (p)        | $10^{-12}$ |

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1A

|          |           |                   |   |           |
|----------|-----------|-------------------|---|-----------|
| <b>1</b> | <b>H</b>  | Hydrogen<br>1.008 | 2 | 2A        |
| 3        | <b>Li</b> | Lithium<br>6.941  | 4 | <b>Be</b> |

| 1A  |           | Atomic number       |     |           |                     |     |           |                     |     |           |                        | 8A        |                 |                       |
|-----|-----------|---------------------|-----|-----------|---------------------|-----|-----------|---------------------|-----|-----------|------------------------|-----------|-----------------|-----------------------|
| 1A  |           | Atomic mass         |     |           |                     |     |           |                     |     |           |                        | 8A        |                 |                       |
| 9   | <b>F</b>  | Fluorine<br>19.00   | 10  | 11        | 12                  | 13  | 14        | 15                  | 16  | 17        | 18                     | <b>He</b> | Helium<br>4.003 |                       |
| 3   | <b>Li</b> | Lithium<br>6.941    | 4   | <b>Be</b> | Beryllium<br>9.012  | 5   | <b>C</b>  | Carbon<br>12.01     | 6   | <b>N</b>  | Nitrogen<br>14.01      | 7         | <b>O</b>        | Oxygen<br>16.00       |
| 11  | <b>Na</b> | Sodium<br>22.99     | 12  | <b>Mg</b> | Magnesium<br>24.31  | 13  | <b>Al</b> | Aluminum<br>26.98   | 14  | <b>Si</b> | Silicon<br>28.09       | 15        | <b>P</b>        | Phosphorus<br>30.97   |
| 19  | <b>K</b>  | Potassium<br>39.10  | 20  | <b>Ca</b> | Calcium<br>40.08    | 21  | <b>Sc</b> | Scandium<br>44.96   | 22  | <b>Ti</b> | Titanium<br>47.88      | 23        | <b>V</b>        | Vanadium<br>50.94     |
| 37  | <b>Rb</b> | Rubidium<br>85.47   | 38  | <b>Sr</b> | Strontrium<br>87.62 | 39  | <b>Zr</b> | Zirconium<br>91.22  | 40  | <b>Nb</b> | Niobium<br>92.91       | 41        | <b>Mo</b>       | Molybdenum<br>95.94   |
| 55  | <b>Cs</b> | Ceasium<br>132.9    | 56  | <b>Ba</b> | Barium<br>137.3     | 57  | <b>La</b> | Lanthanum<br>138.9  | 58  | <b>Hf</b> | Hafnium<br>178.5       | 59        | <b>Ta</b>       | Tantalum<br>180.9     |
| 87  | <b>Fr</b> | Francium<br>(223)   | 88  | <b>Ra</b> | Radium<br>(226)     | 89  | <b>Ac</b> | Actinium<br>(227)   | 90  | <b>Rf</b> | Rutherfordium<br>(257) | 91        | <b>Dy</b>       | Dysprosium<br>(140.1) |
| 199 | <b>Tl</b> | Thallium<br>(204.2) | 200 | <b>Pt</b> | Platinum<br>(196.4) | 201 | <b>Ir</b> | Iridium<br>(102.9)  | 202 | <b>Pd</b> | Palladium<br>(106.4)   | 203       | <b>Ag</b>       | Silver<br>(107.9)     |
| 204 | <b>Os</b> | Osmium<br>(190.2)   | 205 | <b>Re</b> | Rhenium<br>(186.2)  | 206 | <b>W</b>  | Tungsten<br>(183.9) | 207 | <b>Ta</b> | Tantalum<br>(180.9)    | 208       | <b>Os</b>       | Osmium<br>(192.2)     |
| 209 | <b>Hg</b> | Mercury<br>(200.6)  | 210 | <b>Pb</b> | Lead<br>(197.0)     | 211 | <b>Bi</b> | Bismuth<br>(204.4)  | 212 | <b>Te</b> | Tellurium<br>(207.2)   | 213       | <b>At</b>       | Astatine<br>(210)     |
| 214 | <b>Fr</b> | Francium<br>(223)   | 215 | <b>Rg</b> | Rongenium<br>(266)  | 216 | <b>At</b> | Actinum<br>(265)    | 217 | <b>Fr</b> | Francium<br>(269)      | 218       | <b>Xe</b>       | Xenon<br>(131.3)      |
| 219 | <b>Lu</b> | Lutetium<br>(175.0) | 220 | <b>Er</b> | Erbium<br>(167.3)   | 221 | <b>Tm</b> | Thulium<br>(168.9)  | 222 | <b>No</b> | Nobelium<br>(254)      | 223       | <b>Yb</b>       | Ytterbium<br>(173.0)  |
| 224 | <b>Lu</b> | Lutetium<br>(257)   | 225 | <b>Er</b> | Erbium<br>(253)     | 226 | <b>Tm</b> | Thulium<br>(256)    | 227 | <b>Yb</b> | Ytterbium<br>(254)     | 228       | <b>Lu</b>       | Lutetium<br>(257)     |

|            |
|------------|
| Metals     |
| Metalloids |
| Nonmetals  |

|     |           |                    |     |           |                       |     |           |                    |     |           |                     |     |           |                     |     |           |                    |     |           |                      |     |           |                    |     |           |                      |     |           |                   |     |           |                      |     |           |                      |     |           |                    |     |           |                     |     |           |                   |
|-----|-----------|--------------------|-----|-----------|-----------------------|-----|-----------|--------------------|-----|-----------|---------------------|-----|-----------|---------------------|-----|-----------|--------------------|-----|-----------|----------------------|-----|-----------|--------------------|-----|-----------|----------------------|-----|-----------|-------------------|-----|-----------|----------------------|-----|-----------|----------------------|-----|-----------|--------------------|-----|-----------|---------------------|-----|-----------|-------------------|
| 58  | <b>Ce</b> | Cerium<br>140.1    | 59  | <b>Pr</b> | Praseodymium<br>140.9 | 60  | <b>Nd</b> | Neodymium<br>144.2 | 61  | <b>Pm</b> | Promethium<br>(147) | 62  | <b>Sm</b> | Samarium<br>150.4   | 63  | <b>Eu</b> | Europium<br>152.0  | 64  | <b>Gd</b> | Gadolinium<br>157.3  | 65  | <b>Tb</b> | Terbium<br>158.9   | 66  | <b>Dy</b> | Dysprosium<br>162.5  | 67  | <b>Ho</b> | Holmium<br>164.9  | 68  | <b>Er</b> | Erbium<br>167.3      | 69  | <b>Tm</b> | Thulium<br>168.9     | 70  | <b>Yb</b> | Ytterbium<br>173.0 | 71  | <b>Lu</b> | Lutetium<br>175.0   |     |           |                   |
| 90  | <b>Th</b> | Thorium<br>232.0   | 91  | <b>Pa</b> | Protactinium<br>(231) | 92  | <b>U</b>  | Uranium<br>238.0   | 93  | <b>Np</b> | Neptunium<br>(237)  | 94  | <b>Pm</b> | Plutonium<br>(242)  | 95  | <b>Am</b> | Americium<br>(243) | 96  | <b>Cm</b> | Curium<br>(247)      | 97  | <b>Bk</b> | Berkelium<br>(247) | 98  | <b>Cf</b> | Californium<br>(249) | 99  | <b>Fm</b> | Fermium<br>(254)  | 100 | <b>Md</b> | Mendelevium<br>(253) | 101 | <b>Md</b> | Mendelevium<br>(256) | 102 | <b>No</b> | Nobelium<br>(254)  | 103 | <b>Lr</b> | Lawrencium<br>(257) |     |           |                   |
| 104 | <b>Hf</b> | Hafnium<br>(178.5) | 105 | <b>Dy</b> | Dysprosium<br>(140.1) | 106 | <b>Ho</b> | Holmium<br>164.9   | 107 | <b>Tb</b> | Terbium<br>158.9    | 108 | <b>Dy</b> | Dysprosium<br>162.5 | 109 | <b>Mt</b> | Methylum<br>(266)  | 110 | <b>Ds</b> | Darmstadium<br>(269) | 111 | <b>Rg</b> | Rongenium<br>(272) | 112 | <b>Fr</b> | Francium<br>(223)    | 113 | <b>Fr</b> | Francium<br>(223) | 114 | <b>Fr</b> | Francium<br>(223)    | 115 | <b>Fr</b> | Francium<br>(223)    | 116 | <b>Fr</b> | Francium<br>(223)  | 117 | <b>Fr</b> | Francium<br>(223)   | 118 | <b>Fr</b> | Francium<br>(223) |

The 1–18 group designation has been recommended by the International Union of Pure and Applied Chemistry (IUPAC) but is not yet in wide use. In this text we use the standard U.S. notation for group numbers (1A–8A and 1B–8B). No names have been assigned for elements 112, 114, and 116. Elements 113, 115, 117, and 118 have not yet been synthesized.

## List of the Elements with Their Symbols and Atomic Masses\*

| Element      | Symbol | Atomic Number | Atomic Mass <sup>†</sup> | Element       | Symbol | Atomic Number | Atomic Mass <sup>†</sup> |
|--------------|--------|---------------|--------------------------|---------------|--------|---------------|--------------------------|
| Actinium     | Ac     | 89            | (227)                    | Mendelevium   | Md     | 101           | (256)                    |
| Aluminum     | Al     | 13            | 26.98                    | Mercury       | Hg     | 80            | 200.6                    |
| Americium    | Am     | 95            | (243)                    | Molybdenum    | Mo     | 42            | 95.94                    |
| Antimony     | Sb     | 51            | 121.8                    | Neodymium     | Nd     | 60            | 144.2                    |
| Argon        | Ar     | 18            | 39.95                    | Neon          | Ne     | 10            | 20.18                    |
| Arsenic      | As     | 33            | 74.92                    | Neptunium     | Np     | 93            | (237)                    |
| Astatine     | At     | 85            | (210)                    | Nickel        | Ni     | 28            | 58.69                    |
| Barium       | Ba     | 56            | 137.3                    | Niobium       | Nb     | 41            | 92.91                    |
| Berkelium    | Bk     | 97            | (247)                    | Nitrogen      | N      | 7             | 14.01                    |
| Beryllium    | Be     | 4             | 9.012                    | Nobelium      | No     | 102           | (253)                    |
| Bismuth      | Bi     | 83            | 209.0                    | Osmium        | Os     | 76            | 190.2                    |
| Bohorium     | Bh     | 107           | (262)                    | Oxygen        | O      | 8             | 16.00                    |
| Boron        | B      | 5             | 10.81                    | Palladium     | Pd     | 46            | 106.4                    |
| Bromine      | Br     | 35            | 79.90                    | Phosphorus    | P      | 15            | 30.97                    |
| Cadmium      | Cd     | 48            | 112.4                    | Platinum      | Pt     | 78            | 195.1                    |
| Calcium      | Ca     | 20            | 40.08                    | Plutonium     | Pu     | 94            | (242)                    |
| Californium  | Cf     | 98            | (249)                    | Polonium      | Po     | 84            | (210)                    |
| Carbon       | C      | 6             | 12.01                    | Potassium     | K      | 19            | 39.10                    |
| Cerium       | Ce     | 58            | 140.1                    | Praseodymium  | Pr     | 59            | 140.9                    |
| Cesium       | Cs     | 55            | 132.9                    | Promethium    | Pm     | 61            | (147)                    |
| Chlorine     | Cl     | 17            | 35.45                    | Protactinium  | Pa     | 91            | (231)                    |
| Chromium     | Cr     | 24            | 52.00                    | Radium        | Ra     | 88            | (226)                    |
| Cobalt       | Co     | 27            | 58.93                    | Radon         | Rn     | 86            | (222)                    |
| Copper       | Cu     | 29            | 63.55                    | Rhenium       | Re     | 75            | 186.2                    |
| Curium       | Cm     | 96            | (247)                    | Rhodium       | Rh     | 45            | 102.9                    |
| Darmstadtium | Ds     | 110           | (269)                    | Roentgenium   | Rg     | 111           | (272)                    |
| Dubnium      | Db     | 105           | (260)                    | Rubidium      | Rb     | 37            | 85.47                    |
| Dysprosium   | Dy     | 66            | 162.5                    | Ruthenium     | Ru     | 44            | 101.1                    |
| Einsteinium  | Es     | 99            | (254)                    | Rutherfordium | Rf     | 104           | (257)                    |
| Erbium       | Er     | 68            | 167.3                    | Samarium      | Sm     | 62            | 150.4                    |
| Europium     | Eu     | 63            | 152.0                    | Scandium      | Sc     | 21            | 44.96                    |
| Fermium      | Fm     | 100           | (253)                    | Seaborgium    | Sg     | 106           | (263)                    |
| Fluorine     | F      | 9             | 19.00                    | Selenium      | Se     | 34            | 78.96                    |
| Francium     | Fr     | 87            | (223)                    | Silicon       | Si     | 14            | 28.09                    |
| Gadolinium   | Gd     | 64            | 157.3                    | Silver        | Ag     | 47            | 107.9                    |
| Gallium      | Ga     | 31            | 69.72                    | Sodium        | Na     | 11            | 22.99                    |
| Germanium    | Ge     | 32            | 72.59                    | Strontium     | Sr     | 38            | 87.62                    |
| Gold         | Au     | 79            | 197.0                    | Sulfur        | S      | 16            | 32.07                    |
| Hafnium      | Hf     | 72            | 178.5                    | Tantalum      | Ta     | 73            | 180.9                    |
| Hassium      | Hs     | 108           | (265)                    | Technetium    | Tc     | 43            | (99)                     |
| Helium       | He     | 2             | 4.003                    | Tellurium     | Te     | 52            | 127.6                    |
| Holmium      | Ho     | 67            | 164.9                    | Terbium       | Tb     | 65            | 158.9                    |
| Hydrogen     | H      | 1             | 1.008                    | Thallium      | Tl     | 81            | 204.4                    |
| Indium       | In     | 49            | 114.8                    | Thorium       | Th     | 90            | 232.0                    |
| Iodine       | I      | 53            | 126.9                    | Thulium       | Tm     | 69            | 168.9                    |
| Iridium      | Ir     | 77            | 192.2                    | Tin           | Sn     | 50            | 118.7                    |
| Iron         | Fe     | 26            | 55.85                    | Titanium      | Ti     | 22            | 47.88                    |
| Krypton      | Kr     | 36            | 83.80                    | Tungsten      | W      | 74            | 183.9                    |
| Lanthanum    | La     | 57            | 138.9                    | Uranium       | U      | 92            | 238.0                    |
| Lawrencium   | Lr     | 103           | (257)                    | Vanadium      | V      | 23            | 50.94                    |
| Lead         | Pb     | 82            | 207.2                    | Xenon         | Xe     | 54            | 131.3                    |
| Lithium      | Li     | 3             | 6.941                    | Ytterbium     | Yb     | 70            | 173.0                    |
| Lutetium     | Lu     | 71            | 175.0                    | Yttrium       | Y      | 39            | 88.91                    |
| Magnesium    | Mg     | 12            | 24.31                    | Zinc          | Zn     | 30            | 65.39                    |
| Manganese    | Mn     | 25            | 54.94                    | Zirconium     | Zr     | 40            | 91.22                    |
| Meitnerium   | Mt     | 109           | (266)                    |               |        |               |                          |

\*All atomic masses have four significant figures. These values are recommended by the Committee on Teaching of Chemistry, International Union of Pure and Applied Chemistry.

<sup>†</sup>Approximate values of atomic masses for radioactive elements are given in parentheses.

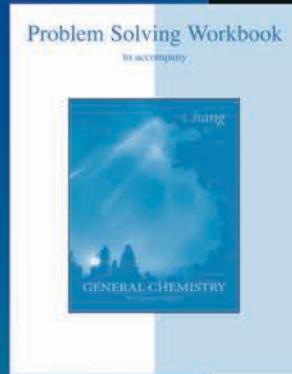


# Chang

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